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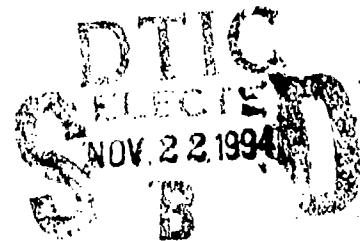TECHNICAL REPORT   AD_____

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GOVERNING EQUATIONS FOR MULTIPHASE HEAT AND MASS TRANSFER IN HYGROSCOPIC POROUS MEDIA WITH APPLICATIONS TO CLOTHING MATERIALS

By
Phillip Gibson

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Whitaker's theory of coupled heat and mass transfer through porous media was modified to include hygroscopic porous materials which can absorb liquid into the solid matrix. The system of equations described in this report should make it possible to evaluate the time-dependent transport properties of hygroscopic and non-hygroscopic clothing materials by including many important factors which are usually ignored in the analysis of heat and mass transfer through textile materials. The set of equations allows for the unsteady capillary wicking of sweat through fabric structure, condensation and evaporation of sweat within various layers of the clothing system, forced gas phase convection through the porous structure of a textile layer, and the swelling and shrinkage of fibers and yarns as they absorb/desorb liquid water and water vapor.

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PREFACE

This report develops a set of nonlinear partial differential equations which describe the coupled transfer of energy and mass through hygroscopic porous media, particularly with reference to textile materials in woven, nonwoven, and laminated forms. The report focuses on the derivation of the equations and their presentation in a form suitable for numerical solution.

This work was undertaken during the preliminary preparation of a doctoral dissertation proposal to the College of Engineering at the University of Massachusetts Lowell. Dr. Majid Charmchi, the author's advisor in the Department of Mechanical Engineering, provided guidance, suggestions, and encouragement during the derivation of the equations given in this report. The two technical reviewers at the U.S. Army Natick Research, Development and Engineering Center were Barry Decristofano of the Science and Advanced Technology Directorate, and Gary Proulx of the Survivability Directorate. These two reviewers provided especially valuable suggestions and comments, and pointed out several errors in the draft version of the report.

SYMBOLS AND ABBREVIATIONS

Roman Letters

A	area [m²]
$a_{\sigma\beta}$	$A_{\sigma\beta}/\mathcal{V}$, surface of the σ–β interface per unit volume [m⁻¹]
$\mathcal{A}_m(t)$	material surface [m²]
c_p	constant pressure heat capacity [J/kg-°K]
C_p	mass fraction weighted average constant pressure heat capacity [J/kg-°K]
$\mathcal{D}$	gas phase molecular diffusivity [m²/sec]
D_a	diffusion coefficient of water vapor in air [m²/sec]
D_{eff}	effective gas phase diffusivity [m²/sec]
$\vec{g}$	gravity vector [m/sec²]
h	enthalpy per unit mass [J/kg]
$h°$	reference enthalpy [J/kg]
$\overline{h}_i$	partial mass enthalpy for the ith species [J/kg]
$h_{\sigma\beta}$	heat transfer coefficient for the σ–β interface [J/sec-m²-°K]
Δh_{vap}	enthalpy of vaporization per unit mass [J/kg]
k	thermal conductivity [J/sec-m-°K]
k_ε	$\partial \langle P_c \rangle / \partial \varepsilon_\beta$ [N/m²]
$k_{\langle T \rangle}$	$\partial \langle P_c \rangle / \partial \langle T \rangle$ [N/m²-°K]
K	permeability coefficient [m²]
K_β	liquid phase permeability tensor [m²/sec]
$\langle \dot{m}_{sl} \rangle$	mass rate of desorption from solid phase to liquid phase per unit volume [kg/sec-m³]

$$\langle \dot{m}_{sl} \rangle = \frac{1}{\mathcal{V}} \int_{A_{\sigma\beta}} \rho_\sigma (\vec{v}_\sigma - \vec{w}_2) \cdot \vec{n}_{\sigma\beta} dA$$

$\langle \dot{m}_{sv} \rangle$	mass rate of desorption from solid phase to vapor phase per unit volume [kg/sec-m³]
$\langle \dot{m}_{lv} \rangle$	mass rate of evaporation per unit volume [kg/sec-m³]
$\vec{n}$	outwardly directed unit normal
p	pressure [N/m²]
P_c	$p_\gamma - p_\beta$, capillary pressure [N/m²]
p_0	reference pressure [N/m²]
$p_1°$	reference vapor pressure for component 1 [N/m²]
Q	volumetric flow rate [m³/sec]
Q_{sl}	enthalpy of desorption from solid phase per unit mass [J/kg]
$\vec{q}$	heat flux vector [J/sec-m²]

$\vec{r}$	position vector [m]
r	characteristic length of a porous media [m]
R_i	gas constant for the ith species [N-m/kg-°K]
T	temperature [°K]
T_0	reference temperature [°K]
T^o	reference temperature [°K]
T	total stress tensor [N/m^2]
t	time [sec]
$\vec{u}_i$	diffusion velocity of the ith species [m/sec]
$\vec{v}$	mass average velocity [m/sec]
$\vec{v}_i$	velocity of the ith species [m/sec]
$V_\sigma(t)$	volume of the solid phase contained within the averaging volume [m^3]
$V_\beta(t)$	volume of the liquid phase contained within the averaging volume [m^3]
$V_\gamma(t)$	volume of the gas phase contained within the averaging volume [m^3]
$\mathcal{V}$	averaging volume [m^3]
$\mathcal{V}_m(t)$	material volume [m^3]
$\vec{w}$	velocity of the β–γ interface [m/sec]
$\vec{w}_1$	velocity of the σ–γ interface [m/sec]
$\vec{w}_2$	velocity of the σ–β interface [m/sec]

Greek Letters

$\varepsilon_\sigma(t)$	$V_\sigma/\mathcal{V}$, volume fraction of the solid phase
$\varepsilon_\beta(t)$	$V_\beta/\mathcal{V}$, volume fraction of the liquid phase
$\varepsilon_\gamma(t)$	$V_\gamma/\mathcal{V}$, volume fraction of the gas phase
$\vec{\xi}$	thermal dispersion vector [J/sec-m^3]
ξ	a function of the topology of the liquid phase
μ	shear coefficient of viscosity [N-sec/m^2]
ρ	density [kg/m^3]
ρ_i	density of the ith species [kg/m^3]
τ	viscous stress tensor [N/m^3]
τ	toruosity factor
Φ	rate of heat generation [J/sec-m^3]
ϕ	p_{vap}/p_{sat}, relative humidity
$\vec{\lambda}$	unit tangent vector

Subscripts

i	designates the ith species in the gas phase
l	liquid
L	liquid
s	solid
S	solid
σ	designates a property of the solid phase
β	designates a property of the liquid phase
γ	designates a property of the gas phase
$\sigma\beta$	designates a property of the σ–β interface
$\sigma\gamma$	designates a property of the σ–γ interface
$\beta\gamma$	designates a property of the β–γ interface

Mathematical Symbols

d/dt	total time derivative
D/Dt	material time derivative
$\partial/\partial t$	partial time derivative
$\langle\psi\rangle$	spatial average of a function ψ which is defined everywhere in space
$\langle\psi_\beta\rangle$	phase average of a function ψ_β which represents a property of the β phase
$\langle\psi_\beta\rangle^\beta$	intrinsic phase average of a function ψ_β which represents a property of the β phase

Governing Equations for Multiphase Heat and Mass Transfer in Hygroscopic Porous Media with Applications to Clothing Materials

1. Introduction

The purpose of this report is to develop a comprehensive set of governing equations which describe the coupled transfer of energy and mass through hygroscopic porous media. The report focuses on the derivation of the equations and their presentation in a form suitable for numerical solution. The various steps of the derivation are presented in sufficient detail so that the origin of each term is clear. The level of detail presented should make it easier to modify each equation according to the requirements of a particular problem or material.

The basis for the set of governing equations is Whitaker's comprehensive theory for mass and energy transport through porous media[1]. These equations are also applicable to mass and energy transport through textile materials if some modifications are made. Whitaker modeled the solid portion of the solid matrix as a rigid inert material which only participates in the transport process through its thermal properties. In hygroscopic textile materials the diffusion of water into the solid is a significant part of the total transport process. The inclusion of the extra transport terms into and out of the solid matrix necessitate extensive modifications of Whitaker's original derivations.

The structure of this report follows Whitaker's derivations as closely as possible. Many references are made to his original derivation. Where possible, the nomenclature and symbols are identical to Whitaker's original derivation to facilitate cross-referencing between this modified set of equations and Whitaker's original set of equations.

2. Mass and Energy Transport Equations

The hygroscopic porous media is modeled as shown below.
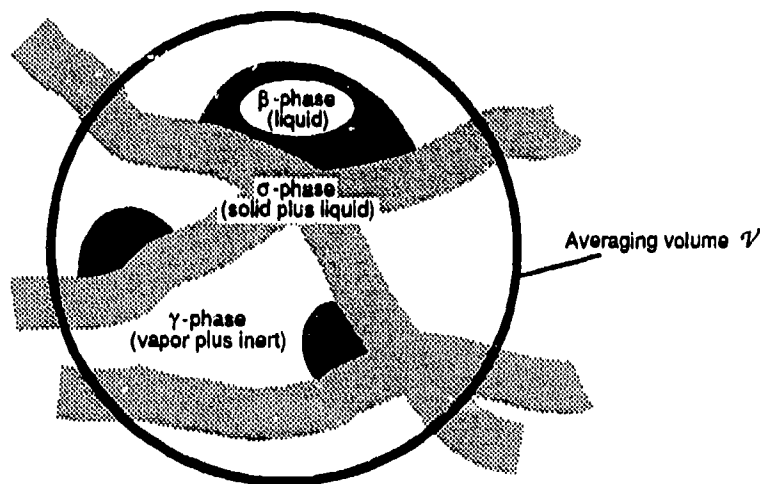
Figure 1. Three phases present in hygroscopic porous media.

A typical porous hygroscopic textile material may be described as a mixture of a solid phase, a liquid phase, and a gaseous phase. The solid σ phase consists of the solid material (usually a polymer e.g. wool or cotton) plus any bound water absorbed in the solid polymer matrix. The solid phase is thus a mixture of the solid and the liquid. This definition of the solid phase means that the density is dependent on the amount of water contained in the solid phase.

The liquid β phase consists of the free liquid water which may be present within the structure of the porous solid. This would also include water which is contained within the pore spaces of the solid but is not sorbed into the polymeric matrix. This liquid β phase is a pure component, and we will be able to assume a constant density for it.

The gaseous γ phase consists of the vapor component of the liquid (water vapor) plus the inert air component. Since it is a mixture of water vapor and air, its density will not be constant, but will be a function of temperature, concentration, etc.

The appropriate general transport and conservation equations to be used are:

continuity equation:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{v}) = 0 \tag{2.1}$$

linear momentum:

$$\rho \frac{D\vec{v}}{Dt} = \rho \vec{g} + \nabla \cdot \mathsf{T} \tag{2.2}$$

thermal energy equation:

$$\rho \frac{Dh}{Dt} = -\nabla \cdot \vec{q} + \frac{Dp}{Dt} + \nabla \vec{v} : \tau + \Phi \tag{2.3}$$

In keeping with Whitaker's derivation, we will neglect the viscous stress tensor

Point Equations

σ-Phase -- Solid

The solid σ phase is made up of the true dry solid (polymer) plus any of the liquid phase or the vapor component of the gas phase which has dissolved into it or adsorbed onto its surface. This may also result in a volume change for the solid σ phase (swelling). The solid is now a mixture of the true dry solid plus the liquid, so we now must account for the two components.

Since swelling is possible, which results in a small velocity of the solid portion due to its displacement, we must account for the velocity of the solid by using the continuity equation:

$$\frac{\partial \rho_\sigma}{\partial t} + \nabla \cdot (\rho_\sigma \vec{v}_\sigma) = 0 \tag{2.4}$$

and for the two components of liquid (1) + solid component (2), the species continuity equation is:

$$\frac{\partial \rho_j}{\partial t} + \nabla \cdot (\rho_j \vec{v}_j) = 0 \quad , \quad i = 1, 2, \ldots \tag{2.5}$$

The σ phase density is not constant, since it includes the density of the solid plus the density of the liquid contained within the solid. The species densities are likewise not constant, since the species density is calculated on the basis of the total phase volume. For the two species:

$$\rho = \frac{m_1 + m_2}{V_\sigma} = \frac{m_1}{V_\sigma} + \frac{m_2}{V_\sigma} = \rho_1 + \rho_2 \tag{2.6}$$

We will assume that the dry density of the solid, and the density of the liquid are constant, and will call them ρ_s and ρ_L.

3

For the solid phase, we can divide the solid phase volume into the fraction taken up by the liquid, and the fraction taken up by the solid:

$$\varepsilon_{\sigma L} = \frac{\text{Volume of Liquid}}{\text{Total } \sigma \text{ Phase Volume}} \qquad (2.7)$$

The relation between the species densities and the solid and liquid densities is:

$$\rho = \varepsilon_{\sigma L}\rho_L + (1 - \varepsilon_{\sigma L})\rho_S = \rho_1 + \rho_2 \qquad (2.8)$$

$$\rho_1 = \varepsilon_{\sigma L}\rho_L \qquad (2.9)$$

$$\rho_2 = (1 - \varepsilon_{\sigma L})\rho_S \qquad (2.10)$$

The density and velocity of the mixture, in terms of the species densities, is given as:

$$\rho_\sigma = \rho_1 + \rho_2 \qquad (2.11)$$

$$\rho_\sigma \vec{v}_\sigma = \rho_1 \vec{v}_1 + \rho_2 \vec{v}_2 \qquad (2.12)$$

or

$$\rho_\sigma = \varepsilon_{\sigma L}\rho_L + (1 - \varepsilon_{\sigma L})\rho_S \qquad (2.13)$$

$$\rho_\sigma \vec{v}_\sigma = \varepsilon_{\sigma L}\rho_L \vec{v}_1 + (1 - \varepsilon_{\sigma L})\rho_S \vec{v}_2 \qquad (2.14)$$

The species velocity is written in terms of the mass average velocity and the diffusion velocity as:

$$\vec{v}_i = \vec{v}_\sigma + \vec{u}_i \qquad (2.15)$$

and the continuity equation becomes:

$$\frac{\partial \rho_i}{\partial t} + \nabla \cdot (\rho_i \vec{v}_\sigma) = -\nabla \cdot (\rho_i \vec{u}_i) \quad , \ i = 1, \ 2, \ 3, \ \dots \qquad (2.16)$$

The diffusion flux may be written in terms of a diffusion coefficient as:

$$\rho_i \vec{u}_i = -\rho_\sigma \mathcal{D}_\sigma \nabla \left(\frac{\rho_i}{\rho_\sigma} \right) \qquad (2.17)$$

and the continuity equation may be written as:

$$\frac{\partial \rho_i}{\partial t} + \nabla \cdot (\rho_i \vec{v}_\sigma) = \nabla \cdot \left\{ \rho_\sigma \mathcal{D}_\sigma \nabla \left(\frac{\rho_i}{\rho_\sigma} \right) \right\} \quad , \ i = 1, \ 2, \ 3, \ \dots \qquad (2.18)$$

For the purposes of comparison to other models of heat and mass transfer through porous materials, it will be convenient later on to write these equations in terms of concentrations of water (component 1) in the solid (component 2).

We define the concentration of water in the solid (C_s) as:

$$C_s = \frac{\text{Mass of water}}{\text{Mass of the solid phase}} = \frac{m_1}{m_1 + m_2} = \frac{\rho_1}{\rho_\sigma} \qquad (2.19)$$

4

If we only want to consider the continuity equation for the liquid phase, since it's really the only material moving into or out of the solid phase, we can just use the continuity equation for the liquid, which is:

$$\frac{\partial \rho_1}{\partial t} + \nabla \cdot (\rho_1 \vec{v}_\sigma) = \nabla \cdot \left\{ \rho_\sigma \mathcal{D}_\sigma \nabla \left(\frac{\rho_1}{\rho_\sigma} \right) \right\} \tag{2.20}$$

Now depending on how we want to treat the solid velocity, we can rewrite this a couple of ways. If we say that the solid velocity is included, then in terms of the true liquid density, where the species density is given by:

$$\rho_1 = \varepsilon_{\sigma L} \rho_L \quad \text{and} \quad \rho_\sigma = \varepsilon_{\sigma L} \rho_L + (1 - \varepsilon_{\sigma L}) \rho_S \,, \tag{2.21}$$

the continuity equation can be rewritten as:

$$\rho_L \left[\frac{\partial \varepsilon_{\sigma L}}{\partial t} + \nabla \cdot (\varepsilon_{\sigma L} \vec{v}_\sigma) \right] = \nabla \cdot \left\{ \rho_\sigma \mathcal{D}_{L\sigma} \nabla (C_s) \right\} \tag{2.22}$$

or

$$\frac{\partial \varepsilon_{\sigma L}}{\partial t} + \nabla \cdot (\varepsilon_{\sigma L} \vec{v}_\sigma) = \left(1 - \frac{\rho_S}{\rho_L} \right) \nabla \cdot \left[\varepsilon_{\sigma L} \mathcal{D}_{L\sigma} \nabla (C_s) \right] + \frac{\rho_S}{\rho_L} \left\{ \nabla \cdot \left[\mathcal{D}_{L\sigma} \nabla (C_s) \right] \right\} \,. \tag{2.23}$$

If we can neglect the solid velocity, the continuity equation becomes:

$$\frac{\partial \varepsilon_{\sigma L}}{\partial t} = \left(1 - \frac{\rho_S}{\rho_L} \right) \nabla \cdot \left[\varepsilon_{\sigma L} \mathcal{D}_{L\sigma} \nabla (C_s) \right] + \frac{\rho_S}{\rho_L} \left\{ \nabla \cdot \left[\mathcal{D}_{L\sigma} \nabla (C_s) \right] \right\} \tag{2.24}$$

We must also include the momentum balance:

$$\rho_\sigma \frac{D \vec{v}_\sigma}{Dt} = \rho_\sigma \vec{g} + \nabla \cdot \mathsf{T}_\sigma \quad \Rightarrow \quad \rho_\sigma \left\{ \frac{\partial \vec{v}_\sigma}{\partial t} + (\vec{v}_\sigma \cdot \nabla) \vec{v}_\sigma \right\} = \rho_\sigma \vec{g} + \nabla \cdot \mathsf{T}_\sigma \tag{2.25}$$

According to Jomaa and Puigali[2], we may also write the linear momentum equation as:

$$\rho_\sigma \frac{\partial \vec{v}_\sigma}{\partial t} = \rho_\sigma \vec{g} + \nabla \cdot \mathsf{T}_\sigma \tag{2.26}$$

5

There are a couple of ways to address the mass average solid phase velocity. If we assume that the total thickness of the materials we are trying to model does not change, then total volume remains constant, and the change in volume of the solid is directly related either to the change in volume of the liquid phase, or the change in volume of the gas phase. Another approach is to let the total volume of the material change with time. As the material dries out, and the total mass changes, the thickness of the material will decrease with time proportional to the water loss which takes place. Allowing the thickness of the material to change with time would result in a solid phase velocity, which we could relate to the total material shrinkage. The two situations are illustrated in Figure 2 for a matrix of solid fibers undergoing shrinkage due to water loss.

Case 1

Solid fiber shrinkage results in bulk thickness reduction and nonzero mass average solid velocity.

Case 2

Total bulk thickness and volume do not change; shrinkage of solid fiber portion due to water loss does not result in a mass average solid velocity.
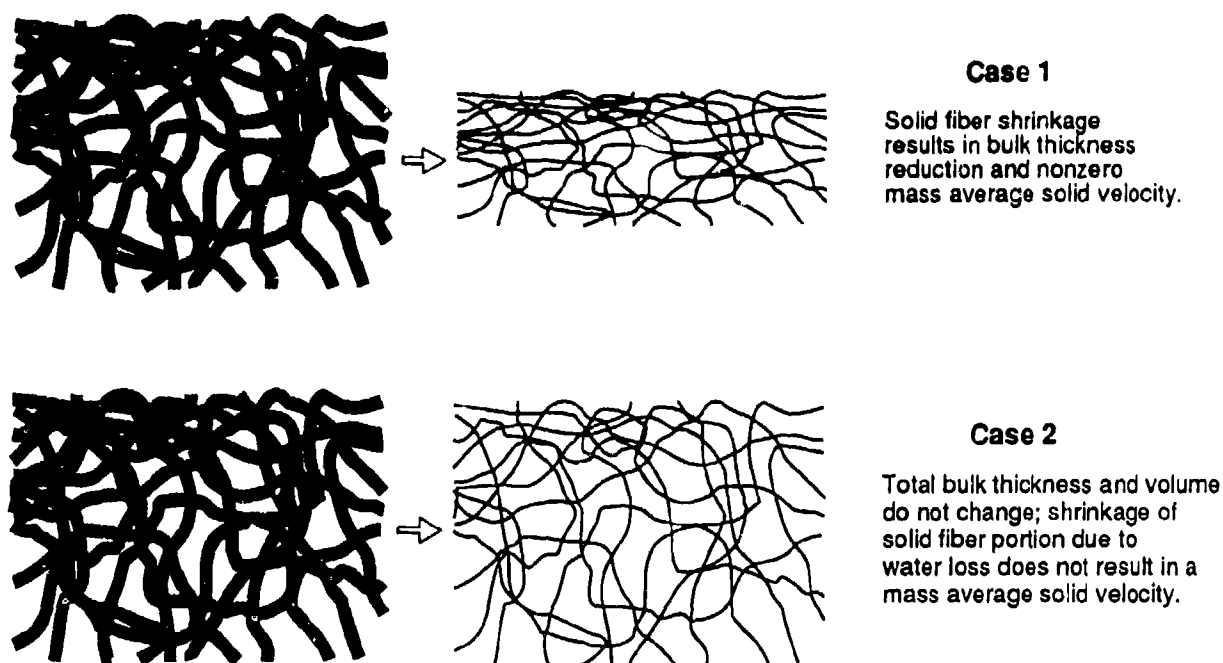
Figure 2. Two methods of accounting for shrinkage/swelling due to water uptake by a porous solid.

We will assume that the shrinkage behavior is like the first case shown. This means that we must include the mass average velocity in the derivations, and that the total material volume (or thickness in one dimension) will no longer remain constant.

Jomaa and Puiggali also give an equation for the solid velocity, in terms of the intrinsic phase average (discussed later) as:

$$\langle v_\sigma \rangle^\sigma = \frac{1}{\langle \rho \rangle^\sigma \xi^{n-1}} \int_0^\xi \frac{\partial}{\partial t} \langle \rho_\sigma \rangle d\xi \tag{2.27}$$

where ξ is the generalized space coordinate, with the origin at the center of symmetry, and n depends on the geometry (n=1--plane, n=2--cylinder, n=3--sphere) according to the paper by Crapiste et. al.[3]

6

The thermal energy equation is:

$$\rho_\sigma \frac{Dh_\sigma}{Dt} = -\nabla \cdot \vec{q}_\sigma + \frac{Dp}{Dt} + \nabla \vec{v}_\sigma : \tau + \Phi_\sigma \qquad (2.28)$$

Some simplifying assumptions can be made at this point by neglecting several effects. We'll start by dropping the reversible and irreversible work terms in the thermal energy equation, along with the source term, and expand the material derivative:

$$\rho_\sigma \frac{Dh_\sigma}{Dt} = \rho_\sigma \left(\frac{\partial h_\sigma}{\partial t} + \vec{v}_\sigma \cdot \nabla h_\sigma \right) = -\nabla \cdot \vec{q}_\sigma \qquad (2.29)$$

It will be assumed that enthalpy is independent of pressure. and is only a function of temperature, and that heat capacity is constant for all the phases.

We can replace the enthalpy by:
$h = c_p T + \text{constant}$, in the σ, β, and γ phases.

We can now rewrite the thermal energy equation as:

$$\rho_\sigma \frac{\partial (c_p)_\sigma T_\sigma}{\partial t} + \rho_\sigma \left[\vec{v}_\sigma \cdot \nabla (c_p)_\sigma T_\sigma + \text{constant} \right] = -\nabla \cdot \vec{q}_\sigma \qquad (2.30)$$

$$\rho_\sigma (c_p)_\sigma \frac{\partial T_\sigma}{\partial t} + \rho_\sigma (c_p)_\sigma \vec{v}_\sigma \cdot \nabla T_\sigma = \rho_\sigma (c_p)_\sigma \left\{ \frac{\partial T_\sigma}{\partial t} + \vec{v}_\sigma \cdot \nabla T_\sigma \right\} = -\nabla \cdot \vec{q}_\sigma \qquad (2.31)$$

We may apply Fourier's law to obtain:

$$\rho_\sigma (c_p)_\sigma \left\{ \frac{\partial T_\sigma}{\partial t} + \vec{v}_\sigma \cdot \nabla T_\sigma \right\} = k_\sigma \nabla^2 T_\sigma \qquad (2.32)$$

or, for a multi-component mixture:

$$\rho_\sigma (c_p)_\sigma \left(\frac{\partial T_\sigma}{\partial t} + \vec{v}_\sigma \cdot \nabla T_\sigma \right) = k_\sigma \nabla^2 T - \nabla \cdot \left(\sum_{j=1}^{j=N} \rho_j \vec{u}_j \bar{h}_j \right) \qquad (2.33)$$

where $(c_p)_\sigma = \sum_{j=1}^{j=N} \frac{\rho_j}{\rho_\sigma} (\bar{c}_p)_j$

and the partial mass heat capacity and enthalpies $(\bar{c}_p)_j$, $\bar{h}_j$ are given by the partial molar enthalpy and the partial molar heat capacity divided by the molecular weight of that component.

β Phase -- Liquid

The continuity equation for the liquid phase is:

$$\frac{\partial \rho_\beta}{\partial t} + \nabla \cdot \left(\rho_\beta \vec{v}_\beta \right) = 0 \tag{2.34}$$

For the thermal energy equation, as we did before, we neglect compressional work and viscous dissipation:

$$\frac{Dp}{Dt} = \nabla \vec{v}_\beta : \tau_\beta = \Phi_\beta = 0 \tag{2.35}$$

which reduces the thermal energy equation to:

$$\rho_\beta \left(\frac{\partial h_\beta}{\partial t} + \vec{v}_\beta \cdot \nabla h_\beta \right) = -\nabla \cdot \vec{q}_\beta \tag{2.36}$$

If we assume enthalpy only depends on temperature and specific heat, as we did for the solid, we may write the thermal energy equation for the liquid phase as:

$$\rho_\beta (c_p)_\beta \left(\frac{\partial T_\beta}{\partial t} + \vec{v}_\beta \cdot \nabla T_\beta \right) = k_\beta \nabla^2 T_\beta \tag{2.37}$$

The liquid momentum equation will be discussed later in terms of a permeability coefficient which depends on the level of liquid saturation in the porous solid.

γ Phase -- Gas

The gas phase is made up of the vapor form of the liquid β phase, and an inert component (air). We do not need to modify any of the assumptions made by Whitaker for this phase, so we may simply write down the equations given by Whitaker[1]:

continuity equation:

$$\frac{\partial \rho_\gamma}{\partial t} + \nabla \cdot \left(\rho_\gamma \vec{v}_\gamma\right) = 0 \tag{2.38}$$

and for the two components of vapor (1) + inert component (2), the species continuity equation is:

$$\frac{\partial \rho_i}{\partial t} + \nabla \cdot \left(\rho_i \vec{v}_i\right) = 0 \quad , \quad i = 1, 2, \ldots \tag{2.39}$$

The density and velocity of the mixture is given as:

$$\rho_\gamma = \rho_1 + \rho_2 \tag{2.40}$$

$$\rho_\gamma \vec{v}_\gamma = \rho_1 \vec{v}_1 + \rho_2 \vec{v}_2 \tag{2.41}$$

The species velocity is written is terms of the mass average velocity and the diffusion velocity as:

$$\vec{v}_i = \vec{v}_\gamma + \vec{u}_i \tag{2.42}$$

and the continuity equation becomes:

$$\frac{\partial \rho_i}{\partial t} + \nabla \cdot \left(\rho_i \vec{v}_\gamma\right) = -\nabla \cdot \left(\rho_i \vec{u}_i\right) \quad , \quad i = 1, 2, 3, \ldots \tag{2.43}$$

The diffusion flux may be written in terms of a diffusion coefficient as:

$$\rho_i \vec{u}_i = -\rho_\gamma \mathcal{D} \nabla \left(\frac{\rho_i}{\rho_\gamma}\right) \tag{2.44}$$

and the continuity equation may be written as:

$$\frac{\partial \rho_i}{\partial t} + \nabla \cdot \left(\rho_i \vec{v}_\gamma\right) = \nabla \cdot \left\{\rho_\gamma \mathcal{D} \nabla \left(\frac{\rho_i}{\rho_\gamma}\right)\right\} \quad , \quad i = 1, 2, 3, \ldots \tag{2.45}$$

It is possible that we can neglect the change in gas density with time, or at least the change in the density of the inert component, and only consider the continuity equation for the vapor component of the gas phase (component 1):

$$\frac{\partial \rho_1}{\partial t} + \nabla \cdot \left(\rho_1 \vec{v}_\gamma\right) = \nabla \cdot \left\{\rho_\gamma \mathcal{D} \nabla \left(\frac{\rho_1}{\rho_\gamma}\right)\right\} \tag{2.46}$$

and if we have no gas phase convection, with the gas phase stagnant in the pore spaces, the continuity equation becomes:

$$\frac{\partial \rho_1}{\partial t} = \nabla \cdot \left\{\rho_\gamma \mathcal{D} \nabla \left(\frac{\rho_1}{\rho_\gamma}\right)\right\} \tag{2.47}$$

The thermal energy equation is given as:

$$\rho_\gamma (c_p)_\gamma \left(\frac{\partial T_\gamma}{\partial t} + \vec{v}_\gamma \cdot \nabla T_\gamma \right) = k_\gamma \nabla^2 T - \nabla \cdot \left(\sum_{i=1}^{i=N} \rho_i \vec{u}_i \bar{h}_i \right) \qquad (2.48)$$

where $(c_p)_\gamma = \sum_{i=1}^{i=N} \frac{\rho_i}{\rho_\gamma} (\bar{c}_p)_i$,

and the partial mass heat capacities and enthalpies $(\bar{c}_p)_i$, $\bar{h}_i$ are again given by the partial molar enthalpy and the partial molar heat capacity divided by the molecular weight of that component.

Boundary Conditions

Whitaker next derives the boundary conditions for each phase interface. This section of the original derivation must be extensively modified since we no longer have a rigid solid phase with zero velocity. We will no longer have a simple set of boundary conditions for the solid-liquid and solid-vapor interface. The conventions and nomenclature for the phase interface boundary conditions are given below in Figure 3, which follows Whitaker's approach as closely as possible.
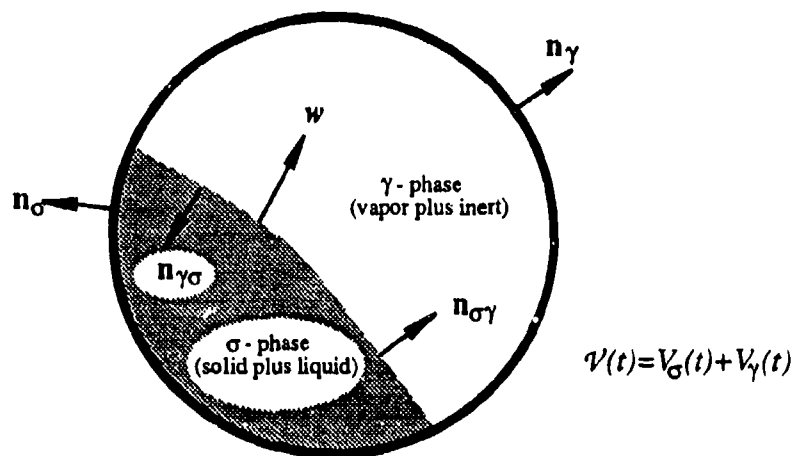

Figure 3. Material volume containing a phase interface, with velocities and unit normals indicated. Only two phases (solid and gas) shown.

Liquid-Gas Boundary Conditions

Whitaker gives the appropriate boundary conditions for the liquid-gas interface as:

$$\rho_\beta h_\beta \left(\vec{v}_\beta - \vec{w} \right) \cdot \vec{n}_{\beta\gamma} + \rho_\gamma h_\gamma \left(\vec{v}_\gamma - \vec{w} \right) \cdot \vec{n}_{\gamma\beta} = - \left\{ \vec{q}_\beta \cdot \vec{n}_{\beta\gamma} + \left[\vec{q}_\gamma + \sum_{i=1}^{i=N} \rho_i \vec{u}_i \bar{h}_i \right] \cdot \vec{n}_{\gamma\beta} \right\} \tag{2.49}$$

$$\rho_\beta \left(\vec{v}_\beta - \vec{w} \right) \cdot \vec{n}_{\beta\gamma} + \rho_\gamma \left(\vec{v}_\gamma - \vec{w} \right) \cdot \vec{n}_{\gamma\beta} = 0 \tag{2.50}$$

continuous tangent components to the phase interface λ:

$$\vec{v}_\beta \cdot \vec{\lambda}_{\beta\gamma} = \vec{v}_\gamma \cdot \vec{\lambda}_{\gamma\beta} \tag{2.51}$$

species jump condition given by:

$$\rho_i \left(\vec{v}_i - \vec{w} \right) \cdot \vec{n}_{\gamma\beta} + \rho_\beta \left(\vec{v}_\beta - \vec{w} \right) \cdot \vec{n}_{\beta\gamma} = 0 \quad , i = 1$$

$$\rho_i \left(\vec{v}_i - \vec{w} \right) \cdot \vec{n}_{\gamma\beta} = 0 \quad , i = 2, 3, \ldots \tag{2.52}$$

$$\tag{2.53}$$

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Solid-Liquid Boundary Conditions

The boundary conditions for the solid-liquid interface are identical except that the phase interface velocity is given by w_2 .

$$\rho_\sigma h_\sigma (\vec{v}_\sigma - \vec{w}_2) \cdot \vec{n}_{\sigma\beta} + \rho_\beta h_\beta (\vec{v}_\beta - \vec{w}_2) \cdot \vec{n}_{\beta\sigma} = -\left\{ \vec{q}_\beta \cdot \vec{n}_{\beta\sigma} + \left[\vec{q}_\sigma + \sum_{j=1}^{j=N} \rho_j \vec{u}_j \vec{h}_j \right] \cdot \vec{n}_{\sigma\beta} \right\} \tag{2.54}$$

$$\rho_\sigma (\vec{v}_\sigma - \vec{w}_2) \cdot \vec{n}_{\sigma\beta} + \rho_\beta (\vec{v}_\beta - \vec{w}_2) \cdot \vec{n}_{\beta\sigma} = 0 \tag{2.55}$$

continuous tangent components to the phase interface λ:

$$\vec{v}_\sigma \cdot \vec{\lambda}_{\sigma\beta} = \vec{v}_\beta \cdot \vec{\lambda}_{\beta\sigma} \tag{2.56}$$

species jump condition given by:

$$\rho_j (\vec{v}_j - \vec{w}_2) \cdot \vec{n}_{\beta\sigma} + \rho_\sigma (\vec{v}_\sigma - \vec{w}_2) \cdot \vec{n}_{\sigma\beta} = 0 \quad , j = 1$$

$$\rho_j (\vec{v}_j - \vec{w}_2) \cdot \vec{n}_{\beta\sigma} = 0 \quad , j = 2, 3, \ldots \tag{2.58}$$

Solid-Gas Boundary Conditions

The boundary conditions for the solid-liquid interface are modified even more because we have a phase interface between two multi-component phases. The phase interface velocity is given by w_1 .

$$\rho_\sigma h_\sigma (\vec{v}_\sigma - \vec{w}_1) \cdot \vec{n}_{\sigma\gamma} + \rho_\gamma h_\gamma (\vec{v}_\gamma - \vec{w}_1) \cdot \vec{n}_{\gamma\sigma} = -\left\{ \left[\vec{q}_\sigma + \sum_{j=1}^{j=N} \rho_j \vec{u}_j \vec{h}_j \right] \cdot \vec{n}_{\sigma\gamma} + \left[\vec{q}_\gamma + \sum_{i=1}^{i=N} \rho_i \vec{u}_i \vec{h}_i \right] \cdot \vec{n}_{\gamma\sigma} \right\} \tag{2.59}$$

$$\rho_\sigma (\vec{v}_\sigma - \vec{w}_1) \cdot \vec{n}_{\sigma\gamma} + \rho_\gamma (\vec{v}_\gamma - \vec{w}_1) \cdot \vec{n}_{\gamma\sigma} = 0 \tag{2.60}$$

continuous tangent components to the phase interface λ:

$$\vec{v}_\sigma \cdot \vec{\lambda}_{\sigma\gamma} = \vec{v}_\gamma \cdot \vec{\lambda}_{\gamma\sigma} \tag{2.61}$$

species jump condition given by:

$$(2.62)$$
$$\rho_j (\vec{v}_j - \vec{w}_1) \cdot \vec{n}_{\sigma\gamma} + \rho_i (\vec{v}_i - \vec{w}_1) \cdot \vec{n}_{\gamma\sigma} = 0 \quad , i = 1 \quad , j = 1 \tag{2.63}$$

$$\rho_j (\vec{v}_j - \vec{w}_1) \cdot \vec{n}_{\sigma\gamma} = 0 \quad , j = 2, 3, \ldots \tag{2.64}$$

$$\rho_i (\vec{v}_i - \vec{w}_1) \cdot \vec{n}_{\gamma\sigma} = 0 \quad , i = 2, 3, \ldots$$

Volume Averaged Equations

Whitaker uses the volume-averaging approach outlined by Slattery[4] so that many of the complicated phenomena going on due to the geometry of the porous material are simplified. He defines three averages:

Spatial Average: Average of some function everywhere in the volume.

$$\langle \psi \rangle = \frac{1}{\mathcal{V}} \int_{\mathcal{V}} \psi dV \tag{2.65}$$

Phase Average: Average of some quantity associated solely with each phase.

$$\langle T_\sigma \rangle = \frac{1}{\mathcal{V}} \int_{\mathcal{V}} T_\sigma dV = \frac{1}{\mathcal{V}} \int_{\mathcal{V}_\sigma} T_\sigma dV \tag{2.66}$$

Intrinsic Phase Average:

$$\langle T_\sigma \rangle^\sigma = \frac{1}{V_\sigma} \int_{\mathcal{V}} T_\sigma dV = \frac{1}{V_\sigma} \int_{\mathcal{V}_\sigma} T_\sigma dV \tag{2.67}$$

We can also define volume fractions for the three phases as:

$$\varepsilon_\sigma(t) = \frac{V_\sigma(t)}{\mathcal{V}} \quad , \quad \varepsilon_\beta(t) = \frac{V_\beta(t)}{\mathcal{V}} \quad , \quad \varepsilon_\gamma(t) = \frac{V_\gamma(t)}{\mathcal{V}} \tag{2.68}$$

We now have the volume and volume fraction of the solid changing with time, which is not the case with Whitaker's original derivation.

We are going to say that the total volume is conserved, or that:

$$\mathcal{V} = V_\sigma(t) + V_\beta(t) + V_\gamma(t) \tag{2.69}$$

The volume fractions for the three phases are related by:

$$\varepsilon_\sigma(t) + \varepsilon_\beta(t) + \varepsilon_\gamma(t) = 1 \tag{2.70}$$

and the phase average and the intrinsic phase averages are related as:

$$\varepsilon_\sigma \langle T_\sigma \rangle^\sigma = \langle T_\sigma \rangle \tag{2.71}$$

Volume Average for Liquid β Phase

We will first look at the volume average for the β phase. It will be complicated because of the three different phase interface velocities which we must now include in the analysis, whereas Whitaker only had to account for the single liquid-gas interface velocity.

The continuity equation for the liquid phase is:

$$\frac{\partial \rho_\beta}{\partial t} + \nabla \cdot \left(\rho_\beta \vec{v}_\beta \right) = 0 \tag{2.72}$$

We will integrate over the time-dependent liquid volume within the averaging volume, and divide by the averaging volume to obtain:

$$\frac{1}{\mathcal{V}} \int_{V_{\beta(t)}} \left(\frac{\partial \rho_\beta}{\partial t} \right) dV + \frac{1}{\mathcal{V}} \int_{V_{\beta(t)}} \nabla \cdot \left(\rho_\beta \vec{v}_\beta \right) dV = 0 \tag{2.73}$$

We may take the first term:

$$\frac{1}{\mathcal{V}} \int_{V_{\beta(t)}} \left(\frac{\partial \rho_\beta}{\partial t} \right) dV \tag{2.74}$$

and apply the general transport theorem[5]:

$$\frac{d}{dt} \int_{V_{(s)}} \psi \, dV = \int_{V_{(s)}} \frac{\partial \psi}{\partial t} dV + \int_{S_{(s)}} \psi \vec{v}_{(s)} \cdot \vec{n} \, dS \tag{2.75}$$

We note that $\Psi = \dfrac{\partial \rho_\beta}{\partial t}$, $\tag{2.76}$

and using the modified general transport theorem we obtain:

$$\frac{1}{\mathcal{V}} \int_{V_{\beta(t)}} \left(\frac{\partial \rho_\beta}{\partial t} \right) dV = \frac{d}{dt} \left[\frac{1}{\mathcal{V}} \int_{V_\beta(t)} \rho_\beta dV \right] - \frac{1}{\mathcal{V}} \int_{A_{\beta\gamma}} \rho_\beta \vec{w} \cdot \vec{n}_{\beta\gamma} dA - \frac{1}{\mathcal{V}} \int_{A_{\beta\sigma}} \rho_\beta \vec{w}_2 \cdot \vec{n}_{\beta\sigma} dA \tag{2.77}$$

For the other term:

$$\frac{1}{\mathcal{V}} \int_{V_{\beta(t)}} \nabla \cdot \left(\rho_\beta \vec{v}_\beta \right) dV \ , \tag{2.78}$$

we may use the volume averaging theorem:

$$\left\langle \nabla \psi_\beta \right\rangle = \nabla \left\langle \psi_\beta \right\rangle + \frac{1}{\mathcal{V}} \int_{A_{\beta\sigma}} \psi_\beta \vec{n}_{\beta\sigma} dA + \frac{1}{\mathcal{V}} \int_{A_{\beta\gamma}} \psi_\beta \vec{n}_{\beta\gamma} dA \tag{2.79}$$

to rewrite the term as:

$$\frac{1}{\mathcal{V}} \int_{V_{\beta(t)}} \nabla \cdot \left(\rho_\beta \vec{v}_\beta \right) dV = \left\langle \nabla \cdot \left(\rho_\beta \vec{v}_\beta \right) \right\rangle = \nabla \cdot \left\langle \rho_\beta \vec{v}_\beta \right\rangle + \frac{1}{\mathcal{V}} \int_{A_{\beta\gamma(t)}} \rho_\beta \vec{v}_\beta \cdot \vec{n}_{\beta\gamma} dA + \frac{1}{\mathcal{V}} \int_{A_{\beta\sigma(t)}} \rho_\beta \vec{v}_\beta \cdot \vec{n}_{\beta\sigma} dA \tag{2.80}$$

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Whitaker says that we may also rewrite the time derivative term as:

$$\frac{d}{dt}\left[\frac{1}{\mathcal{V}}\int_{V_\beta(t)}\rho_\beta dV\right] = \frac{d}{dt}\langle\rho_\beta\rangle = \frac{\partial}{\partial t}\langle\rho_\beta\rangle \tag{2.81}$$

This allows us to rewrite the continuity equation for the liquid phase as:

$$\frac{\partial}{\partial t}\langle\rho_\beta\rangle + \nabla\cdot\langle\rho_\beta\vec{v}_\beta\rangle + \frac{1}{\mathcal{V}}\int_{A_{\beta\gamma}}\rho_\beta\left(\vec{v}_\beta - \vec{w}\right)\cdot\vec{n}_{\beta\gamma}dA + \frac{1}{\mathcal{V}}\int_{A_{\beta\sigma}}\rho_\beta\left(\vec{v}_\beta - \vec{w}_2\right)\cdot\vec{n}_{\beta\sigma}dA = 0 \tag{2.82}$$

We may assume that the density in the liquid is constant, so that:

$$\langle\rho_\beta\vec{v}_\beta\rangle = \rho_\beta\langle\vec{v}_\beta\rangle \tag{2.83}$$

$$\langle\rho_\beta\rangle = \varepsilon_\beta\rho_\beta \tag{2.84}$$

The liquid velocity vector may be used to calculate volumetric flow rates. Whitaker gives the example of the flow rate of the liquid phase past a surface area as:

$$Q_\beta = \int_A\langle\vec{v}_\beta\rangle\cdot\vec{n}dA \tag{2.85}$$

The two constant-density liquid relations given above allow the liquid phase continuity equation to be rewritten as:

$$\frac{\partial\varepsilon_\beta}{\partial t} + \nabla\cdot\langle\vec{v}_\beta\rangle + \frac{1}{\mathcal{V}}\int_{A_{\beta\gamma}}\left(\vec{v}_\beta - \vec{w}\right)\cdot\vec{n}_{\beta\gamma}dA + \frac{1}{\mathcal{V}}\int_{A_{\beta\sigma}}\left(\vec{v}_\beta - \vec{w}_2\right)\cdot\vec{n}_{\beta\sigma}dA = 0 \tag{2.86}$$

The thermal energy equation for the liquid phase was given previously as:

$$\rho_\beta\left(\frac{\partial h_\beta}{\partial t} + \vec{v}_\beta\cdot\nabla h_\beta\right) = -\nabla\cdot\vec{q}_\beta \tag{2.87}$$

Whitaker notes that this may be rewritten by adding the term $h_\beta\left[\frac{\partial\rho_\beta}{\partial t} + \nabla\cdot\left(\rho_\beta\vec{v}_\beta\right)\right]$ to the left-hand side to get:

$$\frac{\partial}{\partial t}\left(\rho_\beta h_\beta\right) + \nabla\cdot\left(\rho_\beta h_\beta\vec{v}_\beta\right) = -\nabla\cdot\vec{q}_\beta \tag{2.88}$$

We may follow the same procedure used previously to obtain a volume averaged form of the thermal energy equation where we use the general transport theorem for the first term and the averaging theorem for the second and third terms to get:

$$\frac{\partial}{\partial t}\left\langle \rho_\beta h_\beta \right\rangle + \nabla \cdot \left\langle \rho_\beta h_\beta \vec{v}_\beta \right\rangle + \frac{1}{\mathcal{V}}\int_{A_{\beta\gamma}} \rho_\beta h_\beta \left(\vec{v}_\beta - \vec{w}\right)\cdot \vec{n}_{\beta\gamma}dA + \frac{1}{\mathcal{V}}\int_{A_{\beta\sigma}} \rho_\beta h_\beta \left(\vec{v}_\beta - \vec{w}_2\right)\cdot \vec{n}_{\beta\sigma}dA$$

$$= -\nabla \cdot \left\langle \vec{q}_\beta \right\rangle + \left\langle \Phi_\beta \right\rangle - \frac{1}{\mathcal{V}}\int_{A_{\beta\gamma}} \vec{q}_\beta \cdot \vec{n}_{\beta\gamma}dA - \frac{1}{\mathcal{V}}\int_{A_{\beta\sigma}} \vec{q}_\beta \cdot \vec{n}_{\beta\sigma}dA \tag{2.89}$$

All we did here was add an additional term to Whitaker's equations due to the solid-liquid interface velocity.

Whitaker uses the relation for the enthalpy of the liquid phase:

$$h_\beta = h_\beta{}^\circ + (c_p)_\beta\left(T_\beta - T_\beta{}^\circ\right) \tag{2.90}$$

and goes through several steps, accounting for the deviation and dispersion terms from the average properties (marked with a tilde), to write an expression for the two terms:

$$\frac{\partial}{\partial t}\left\langle \rho_\beta h_\beta \right\rangle + \nabla \cdot \left\langle \rho_\beta h_\beta \vec{v}_\beta \right\rangle = \varepsilon_\beta \rho_\beta (c_p)_\beta \frac{\partial \left\langle T_\beta \right\rangle^\beta}{\partial t} + \rho_\beta\left[h_\beta{}^\circ + (c_p)_\beta\left(\left\langle T_\beta \right\rangle^\beta - T_\beta{}^\circ\right)\right]\left(\frac{\partial \varepsilon_\beta}{\partial t} + \nabla \cdot \left\langle \vec{v}_\beta \right\rangle\right)$$

$$+ \rho_\beta (c_p)_\beta \left\langle \vec{v}_\beta \right\rangle \cdot \nabla \left\langle T_\beta \right\rangle^\beta + \rho_\beta (c_p)_\beta \nabla \cdot \left\langle \tilde{T}_\beta \tilde{\vec{v}}_\beta \right\rangle \tag{2.91}$$

We can recognize that the term: $\left(\dfrac{\partial \varepsilon_\beta}{\partial t} + \nabla \cdot \left\langle \vec{v}_\beta \right\rangle\right)$

is contained in the liquid phase continuity equation:

$$\left(\frac{\partial \varepsilon_\beta}{\partial t} + \nabla \cdot \left\langle \vec{v}_\beta \right\rangle\right) + \frac{1}{\mathcal{V}}\int_{A_{\beta\gamma}} \left(\vec{v}_\beta - \vec{w}\right)\cdot \vec{n}_{\beta\gamma}dA + \frac{1}{\mathcal{V}}\int_{A_{\beta\sigma}} \left(\vec{v}_\beta - \vec{w}_2\right)\cdot \vec{n}_{\beta\sigma}dA = 0 \tag{2.92}$$

so that:

$$\frac{\partial \varepsilon_\beta}{\partial t} + \nabla \cdot \left\langle \vec{v}_\beta \right\rangle = -\left\{\frac{1}{\mathcal{V}}\int_{A_{\beta\gamma}} \left(\vec{v}_\beta - \vec{w}\right)\cdot \vec{n}_{\beta\gamma}dA + \frac{1}{\mathcal{V}}\int_{A_{\beta\sigma}} \left(\vec{v}_\beta - \vec{w}_2\right)\cdot \vec{n}_{\beta\sigma}dA\right\} \tag{2.93}$$

The expression for the two terms $\dfrac{\partial}{\partial t}\left\langle \rho_\beta h_\beta \right\rangle + \nabla \cdot \left\langle \rho_\beta h_\beta \vec{v}_\beta \right\rangle$ may be written as:

$$\frac{\partial}{\partial t}\left\langle \rho_\beta h_\beta \right\rangle + \nabla \cdot \left\langle \rho_\beta h_\beta \vec{v}_\beta \right\rangle = \varepsilon_\beta \rho_\beta (c_p)_\beta \frac{\partial \left\langle T_\beta \right\rangle^\beta}{\partial t} + \rho_\beta (c_p)_\beta \left\langle \vec{v}_\beta \right\rangle \cdot \nabla \left\langle T_\beta \right\rangle^\beta + \rho_\beta (c_p)_\beta \nabla \cdot \left\langle \tilde{T}_\beta \tilde{\vec{v}}_\beta \right\rangle$$

$$- \left[h_\beta{}^\circ + (c_p)_\beta\left(\left\langle T_\beta \right\rangle^\beta - T_\beta{}^\circ\right)\right]\left\{\frac{1}{\mathcal{V}}\int_{A_{\beta\gamma}} \rho_\beta\left(\vec{v}_\beta - \vec{w}\right)\cdot \vec{n}_{\beta\gamma}dA + \frac{1}{\mathcal{V}}\int_{A_{\beta\sigma}} \rho_\beta\left(\vec{v}_\beta - \vec{w}_2\right)\cdot \vec{n}_{\beta\sigma}dA\right\} \tag{2.94}$$

We may now substitute back into the thermal energy equation for the liquid phase:

$$\varepsilon_\beta \rho_\beta (c_p)_\beta \frac{\partial \langle T_\beta \rangle^\beta}{\partial t} + \rho_\beta (c_p)_\beta \langle \vec{v}_\beta \rangle \cdot \nabla \langle T_\beta \rangle^\beta + \rho_\beta (c_p)_\beta \nabla \cdot \langle \tilde{T}_\beta \tilde{\vec{v}}_\beta \rangle$$

$$+ \frac{1}{\mathcal{V}} \int_{A_{\beta\gamma}} \rho_\beta (c_p)_\beta (T_\beta - T_\beta^\circ)(\vec{v}_\beta - \vec{w}) \cdot \vec{n}_{\beta\gamma} \, dA$$

$$+ \frac{1}{\mathcal{V}} \int_{A_{\beta\sigma}} \rho_\beta (c_p)_\beta (T_\beta - T_\beta^\circ)(\vec{v}_\beta - \vec{w}_2) \cdot \vec{n}_{\beta\sigma} \, dA$$

$$- \frac{1}{\mathcal{V}} \int_{A_{\beta\gamma}} \rho_\beta (c_p)_\beta \left(\langle T_\beta \rangle^\beta - T_\beta^\circ \right)(\vec{v}_\beta - \vec{w}) \cdot \vec{n}_{\beta\gamma} \, dA$$

$$- \frac{1}{\mathcal{V}} \int_{A_{\beta\sigma}} \rho_\beta (c_p)_\beta \left(\langle T_\beta \rangle^\beta - T_\beta^\circ \right)(\vec{v}_\beta - \vec{w}_2) \cdot \vec{n}_{\beta\sigma} \, dA$$

$$= -\nabla \cdot \langle \vec{q}_\beta \rangle + \langle \Phi_\beta \rangle - \frac{1}{\mathcal{V}} \int_{A_{\beta\gamma}} \vec{q}_\beta \cdot \vec{n}_{\beta\gamma} \, dA - \frac{1}{\mathcal{V}} \int_{A_{\beta\sigma}} \vec{q}_\beta \cdot \vec{n}_{\beta\sigma} \, dA \qquad (2.95)$$

Whitaker now uses Gray's definitions of the point functions for the phase properties[6] as:

$$T_\beta = \langle T_\beta \rangle^\beta + \tilde{T}_\beta \qquad (2.96)$$

This allows the liquid phase thermal energy equation to be written as:

$$\varepsilon_\beta \rho_\beta (c_p)_\beta \frac{\partial \langle T_\beta \rangle^\beta}{\partial t} + \rho_\beta (c_p)_\beta \langle \vec{v}_\beta \rangle \cdot \nabla \langle T_\beta \rangle^\beta + \rho_\beta (c_p)_\beta \nabla \cdot \langle \tilde{T}_\beta \tilde{\vec{v}}_\beta \rangle$$

$$+ \frac{1}{\mathcal{V}} \int_{A_{\beta\gamma}} \rho_\beta (c_p)_\beta \tilde{T}_\beta (\vec{v}_\beta - \vec{w}) \cdot \vec{n}_{\beta\gamma} \, dA$$

$$+ \frac{1}{\mathcal{V}} \int_{A_{\beta\sigma}} \rho_\beta (c_p)_\beta \tilde{T}_\beta (\vec{v}_\beta - \vec{w}_2) \cdot \vec{n}_{\beta\sigma} \, dA$$

$$= -\nabla \cdot \langle \vec{q}_\beta \rangle + \langle \Phi_\beta \rangle - \frac{1}{\mathcal{V}} \int_{A_{\beta\gamma}} \vec{q}_\beta \cdot \vec{n}_{\beta\gamma} \, dA - \frac{1}{\mathcal{V}} \int_{A_{\beta\sigma}} \vec{q}_\beta \cdot \vec{n}_{\beta\sigma} \, dA \qquad (2.97)$$

Whitaker now rewrites the heat flux term $-\nabla \cdot \langle \vec{q}_\beta \rangle$ using Fourier's law ($\vec{q}_\beta = -k_\beta \nabla T_\beta$) and the averaging theorem to write:

$$\langle \vec{q}_\beta \rangle = -k_\beta \langle \nabla T_\beta \rangle = -k_\beta \left[\nabla \langle T_\beta \rangle + \frac{1}{\mathcal{V}} \int_{A_{\beta\sigma}} T_\beta \vec{n}_{\beta\sigma} \, dA + \frac{1}{\mathcal{V}} \int_{A_{\beta\gamma}} T_\beta \vec{n}_{\beta\gamma} \, dA \right] \qquad (2.98)$$

We may also substitute the intrinsic phase average temperature $\varepsilon_\beta \langle T_\beta \rangle^\beta$

for the phase average temperature $\langle T_\beta \rangle$ to obtain an expression for the heat flux vector:

$$\langle \vec{q}_\beta \rangle = -k_\beta \langle \nabla T_\beta \rangle = -k_\beta \left[\nabla \left(\varepsilon_\beta \langle T_\beta \rangle^\beta \right) + \frac{1}{\mathcal{V}} \int_{A_{\beta\sigma}} T_\beta \vec{n}_{\beta\sigma} dA + \frac{1}{\mathcal{V}} \int_{A_{\beta\gamma}} T_\beta \vec{n}_{\beta\gamma} dA \right] \qquad (2.99)$$

The thermal energy equation for the liquid phase may now be written as:

$$\varepsilon_\beta \rho_\beta (c_p)_\beta \frac{\partial \langle T_\beta \rangle^\beta}{\partial t} + \rho_\beta (c_p)_\beta \langle \vec{v}_\beta \rangle \cdot \nabla \langle T_\beta \rangle^\beta + \rho_\beta (c_p)_\beta \nabla \cdot \langle \tilde{T}_\beta \tilde{\vec{v}}_\beta \rangle$$

$$+ \frac{1}{\mathcal{V}} \int_{A_{\beta\gamma}} \rho_\beta (c_p)_\beta \tilde{T}_\beta \left(\vec{v}_\beta - \vec{w} \right) \cdot \vec{n}_{\beta\gamma} dA + \frac{1}{\mathcal{V}} \int_{A_{\beta\sigma}} \rho_\beta (c_p)_\beta \tilde{T}_\beta \left(\vec{v}_\beta - \vec{w}_2 \right) \cdot \vec{n}_{\beta\sigma} dA$$

$$= \nabla \cdot \left\{ k_\beta \left[\nabla \left(\varepsilon_\beta \langle T_\beta \rangle^\beta \right) + \frac{1}{\mathcal{V}} \int_{A_{\beta\sigma}} T_\beta \vec{n}_{\beta\sigma} dA + \frac{1}{\mathcal{V}} \int_{A_{\beta\gamma}} T_\beta \vec{n}_{\beta\gamma} dA \right] \right\}$$

$$- \frac{1}{\mathcal{V}} \int_{A_{\beta\gamma}} \vec{q}_\beta \cdot \vec{n}_{\beta\gamma} dA - \frac{1}{\mathcal{V}} \int_{A_{\beta\sigma}} \vec{q}_\beta \cdot \vec{n}_{\beta\sigma} dA \qquad (2.100)$$

Volume Average for Gas γ Phase

The gas phase continuity equation is identical, up to a point, to the continuity equations for the solid and liquid phases:

$$\frac{\partial}{\partial t}\langle\rho_\gamma\rangle+\nabla\cdot\langle\rho_\gamma\vec{v}_\gamma\rangle+\frac{1}{\mathcal{V}}\int_{A_{\gamma\beta}}\rho_\gamma(\vec{v}_\gamma-\vec{w})\cdot\vec{n}_{\gamma\beta}dA+\frac{1}{\mathcal{V}}\int_{A_{\gamma\sigma}}\rho_\gamma(\vec{v}_\gamma-\vec{w}_1)\cdot\vec{n}_{\gamma\sigma}dA=0 \qquad (2.101)$$

For the liquid and solid phases we could assume constant density, and simplify the equation further; we can't do this for the gas phase since the density depends on the temperature and the pressure.

Whitaker uses the Gray's expressions for the point functions again, along with the definition of the intrinsic phase average to rewrite the gas phase continuity equation as:

$$\frac{\partial}{\partial t}\left(\varepsilon_\gamma\langle\rho_\gamma\rangle^\gamma\right)+\nabla\cdot\left(\langle\rho_\gamma\rangle^\gamma\langle\vec{v}_\gamma\rangle\right)+\nabla\cdot\langle\tilde{\rho}_\gamma\tilde{\vec{v}}_\gamma\rangle$$

$$+\frac{1}{\mathcal{V}}\int_{A_{\gamma\beta}}\rho_\gamma(\vec{v}_\gamma-\vec{w})\cdot\vec{n}_{\gamma\beta}dA+\frac{1}{\mathcal{V}}\int_{A_{\gamma\sigma}}\rho_\gamma(\vec{v}_\gamma-\vec{w}_1)\cdot\vec{n}_{\gamma\sigma}dA=0 \qquad (2.102)$$

Whitaker then assumes we can neglect terms with products of the dispersion or deviations, so we can drop that term to write the gas phase continuity equation as:

$$\frac{\partial}{\partial t}\left(\varepsilon_\gamma\langle\rho_\gamma\rangle^\gamma\right)+\nabla\cdot\left(\langle\rho_\gamma\rangle^\gamma\langle\vec{v}_\gamma\rangle\right)+\frac{1}{\mathcal{V}}\int_{A_{\gamma\beta}}\rho_\gamma(\vec{v}_\gamma-\vec{w})\cdot\vec{n}_{\gamma\beta}dA+\frac{1}{\mathcal{V}}\int_{A_{\gamma\sigma}}\rho_\gamma(\vec{v}_\gamma-\vec{w}_1)\cdot\vec{n}_{\gamma\sigma}dA=0 \quad (2.103)$$

Since the gas is a multi-component mixture we must also go through the species continuity equation:

$$\frac{\partial}{\partial t}\langle\rho_i\rangle+\nabla\cdot\langle\rho_i\vec{v}_i\rangle+\frac{1}{\mathcal{V}}\int_{A_{\gamma\beta}}\rho_i(\vec{v}_i-\vec{w})\cdot\vec{n}_{\gamma\beta}dA+\frac{1}{\mathcal{V}}\int_{A_{\gamma\sigma}}\rho_i(\vec{v}_i-\vec{w}_1)\cdot\vec{n}_{\gamma\sigma}dA=0 \qquad i=1,2,\ldots \quad (2.104)$$

Whitaker's derivations may be used directly, and we can write the final form of the gas phase species continuity equation as:

$$\frac{\partial}{\partial t}\left(\varepsilon_\gamma\langle\rho_i\rangle^\gamma\right)+\nabla\cdot\left(\langle\rho_i\rangle^\gamma\langle\vec{v}_i\rangle\right)+\frac{1}{\mathcal{V}}\int_{A_{\gamma\beta}}\rho_i(\vec{v}_i-\vec{w})\cdot\vec{n}_{\gamma\beta}dA+\frac{1}{\mathcal{V}}\int_{A_{\gamma\sigma}}\rho_i(\vec{v}_i-\vec{w}_1)\cdot\vec{n}_{\gamma\sigma}dA \qquad (2.105)$$

If we neglect the deviation terms, and if we also consider only the species continuity equation for the vapor component (component 1), we can rewrite the gas phase continuity equation as:

$$\frac{\partial}{\partial t}\left(\varepsilon_\gamma\langle\rho_1\rangle^\gamma\right)+\nabla\cdot\left(\langle\rho_1\rangle^\gamma\langle\vec{v}_\gamma\rangle\right)+\frac{1}{\mathcal{V}}\int_{A_{\gamma\beta}}\rho_1(\vec{v}_1-\vec{w})\cdot\vec{n}_{\gamma\beta}dA=\nabla\cdot\left\{\langle\rho_\gamma\rangle^\gamma\mathcal{D}\nabla\left(\frac{\rho_1}{\langle\rho_\gamma\rangle^\gamma}\right)\right\} \qquad (2.106)$$

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The corresponding thermal energy equation for the gas phase may also be written as:

$$\left\{\sum_{i=1}^{i=N}\langle\rho_i\rangle(c_p)_i\right\}\frac{\partial\langle T_\gamma\rangle^\gamma}{\partial t}+\left\{\sum_{i=1}^{i=N}(c_p)_i\langle\rho_i\vec{v}_i\rangle\right\}\cdot\nabla\langle T_\gamma\rangle^\gamma$$

$$+\frac{1}{\mathcal{V}}\int_{A_{\gamma\beta}}\sum_{i=1}^{i=N}\rho_i(c_p)_i\tilde{T}_\gamma(\vec{v}_i-\vec{w})\cdot\vec{n}_{\gamma\beta}dA$$

$$+\frac{1}{\mathcal{V}}\int_{A_{\gamma\sigma}}\sum_{i=1}^{i=N}\rho_i(c_p)_i\tilde{T}_\gamma(\vec{v}_i-\vec{w}_1)\cdot\vec{n}_{\gamma\sigma}dA$$

$$+\frac{\partial}{\partial t}\sum_{i=1}^{i=N}(c_p)_i\langle\tilde{\rho}_i\tilde{T}_\gamma\rangle+\nabla\cdot\sum_{i=1}^{i=N}(c_p)_i\langle\tilde{\rho}_i\vec{v}_i\tilde{T}_\gamma\rangle$$

$$=\nabla\cdot\left\{k_\gamma\left[\nabla\left(\varepsilon_\gamma\langle T_\gamma\rangle^\gamma\right)+\frac{1}{\mathcal{V}}\int_{A_{\gamma\sigma}}T_\gamma\vec{n}_{\gamma\sigma}dA+\frac{1}{\mathcal{V}}\int_{A_{\gamma\beta}}T_\gamma\vec{n}_{\gamma\beta}dA\right]\right\}$$

$$-\frac{1}{\mathcal{V}}\int_{A_{\gamma\sigma}}\vec{q}_\gamma\cdot\vec{n}_{\gamma\sigma}dA-\frac{1}{\mathcal{V}}\int_{A_{\gamma\beta}}\vec{q}_\gamma\cdot\vec{n}_{\gamma\beta}dA \tag{2.107}$$

Volume Average for Solid σ Phase

The volume averaging procedure for the liquid phase was made general enough so that the same equations also apply for the solid phase. The only differences are that now the phase interface velocities are w_2 for the solid-liquid interface, and w_1 for the solid-gas interface. We also need to account for the species continuity equations. Since the two components (liquid and the solid) are assumed to have a constant density, we will not run into the same complications we did with the gas phase continuity equation. The appropriate subscripts for the solid phase also need to be added to the equations.

We cannot assume that the solid phase density is constant, since it is a mixture of the solid and the liquid component. However, it will be less complicated than the gas phase density since we can assume that each component's density is constant.

The solid phase continuity equation is:

$$\frac{\partial}{\partial t}\langle\rho_\sigma\rangle + \nabla\cdot\langle\rho_\sigma\vec{v}_\sigma\rangle + \frac{1}{\mathcal{V}}\int_{A_{\sigma\gamma}}(\vec{v}_\sigma - \vec{w}_1)\cdot\vec{n}_{\sigma\gamma}dA + \frac{1}{\mathcal{V}}\int_{A_{\sigma\beta}}(\vec{v}_\sigma - \vec{w}_2)\cdot\vec{n}_{\sigma\beta}dA = 0 \qquad (2.108)$$

and the species continuity equation is:

$$\frac{\partial}{\partial t}\langle\rho_j\rangle + \nabla\cdot\langle\rho_j\vec{v}_j\rangle + \frac{1}{\mathcal{V}}\int_{A_{\sigma\gamma}}(\vec{v}_j - \vec{w}_1)\cdot\vec{n}_{\sigma\gamma}dA + \frac{1}{\mathcal{V}}\int_{A_{\sigma\beta}}(\vec{v}_j - \vec{w}_2)\cdot\vec{n}_{\sigma\beta}dA = 0 \quad j = 1, 2, \ldots \qquad (2.109)$$

We can follow the same derivation used for the gas phase to write the gas phase continuity equation as:

$$\frac{\partial}{\partial t}\left(\varepsilon_\sigma\langle\rho_\sigma\rangle^\sigma\right) + \nabla\cdot\left(\langle\rho_\sigma\rangle^\sigma\langle\vec{v}_\sigma\rangle\right) + \frac{1}{\mathcal{V}}\int_{A_{\sigma\beta}}\rho_\sigma(\vec{v}_\sigma - \vec{w}_2)\cdot\vec{n}_{\sigma\beta}dA + \frac{1}{\mathcal{V}}\int_{A_{\sigma\gamma}}\rho_\sigma(\vec{v}_\sigma - \vec{w}_1)\cdot\vec{n}_{\sigma\gamma}dA = 0 \quad (2.110)$$

and the final form of the solid phase species continuity equation is:

$$\frac{\partial}{\partial t}\left(\varepsilon_\sigma\langle\rho_j\rangle^\sigma\right) + \nabla\cdot\left(\langle\rho_j\rangle^\sigma\langle\vec{v}_j\rangle\right) + \frac{1}{\mathcal{V}}\int_{A_{\sigma\beta}}\rho_j(\vec{v}_j - \vec{w}_2)\cdot\vec{n}_{\sigma\beta}dA + \frac{1}{\mathcal{V}}\int_{A_{\sigma\gamma}}\rho_j(\vec{v}_j - \vec{w}_1)\cdot\vec{n}_{\sigma\gamma}dA$$

$$= \nabla\cdot\left\{\langle\rho_\sigma\rangle^\sigma\mathcal{D}_\sigma\left[\nabla\left(\frac{\rho_j}{\langle\rho_\sigma\rangle^\sigma}\right)\right] - \langle\tilde{\rho}_j\tilde{\vec{v}}_j\rangle\right\} \qquad j = 1, 2, \ldots \qquad (2.111)$$

If we want to just follow the single liquid component (component 1) and write the continuity equation for that species, we may write:

$$\frac{\partial}{\partial t}\left(\varepsilon_\sigma\langle\rho_1\rangle^\sigma\right) + \nabla\cdot\left(\langle\rho_1\rangle^\sigma\langle\vec{v}_1\rangle\right) + \frac{1}{\mathcal{V}}\int_{A_{\sigma\beta}}\rho_1(\vec{v}_1 - \vec{w}_2)\cdot\vec{n}_{\sigma\beta}dA + \frac{1}{\mathcal{V}}\int_{A_{\sigma\gamma}}\rho_1(\vec{v}_1 - \vec{w}_1)\cdot\vec{n}_{\sigma\gamma}dA$$

$$= \nabla\cdot\left\{\langle\rho_\sigma\rangle^\sigma\mathcal{D}_\sigma\nabla\left(\frac{\rho_1}{\langle\rho_\sigma\rangle^\sigma}\right)\right\} \qquad (2.112)$$

Later on, we may also want to assume that the solid velocity is zero, so we could rewrite the solid phase continuity equation as:

$$\frac{\partial}{\partial t}\left(\varepsilon_\sigma\langle\rho_1\rangle^\sigma\right)+\frac{1}{\mathcal{V}}\int_{A_{\sigma\beta}}\rho_1\left(\vec{v}_1-\vec{w}_2\right)\cdot\vec{n}_{\sigma\beta}dA+\frac{1}{\mathcal{V}}\int_{A_{\sigma\gamma}}\rho_1\left(\vec{v}_1-\vec{w}_1\right)\cdot\vec{n}_{\sigma\gamma}dA$$

$$=\nabla\cdot\left\{\langle\rho_\sigma\rangle^\sigma\mathcal{D}_\sigma\nabla\left(\frac{\rho_1}{\langle\rho_\sigma\rangle^\sigma}\right)\right\} \tag{2.113}$$

The corresponding thermal energy equation for the solid phase may also be written as:

$$\left\{\sum_{j=1}^{j=N}\langle\rho_j\rangle(c_p)_j\right\}\frac{\partial\langle T_\sigma\rangle^\sigma}{\partial t}+\left\{\sum_{j=1}^{j=N}(c_p)_j\langle\rho_j\vec{v}_j\rangle\right\}\cdot\nabla\langle T_\sigma\rangle^\sigma$$

$$+\frac{1}{\mathcal{V}}\int_{A_{\sigma\beta}}\sum_{j=1}^{j=N}\rho_j(c_p)_j\tilde{T}_\sigma\left(\vec{v}_j-\vec{w}_2\right)\cdot\vec{n}_{\sigma\beta}dA$$

$$+\frac{1}{\mathcal{V}}\int_{A_{\sigma\gamma}}\sum_{j=1}^{j=N}\rho_j(c_p)_j\tilde{T}_\sigma\left(\vec{v}_j-\vec{w}_1\right)\cdot\vec{n}_{\sigma\gamma}dA$$

$$+\frac{\partial}{\partial t}\sum_{j=1}^{j=N}(c_p)_j\langle\tilde{\rho}_j\tilde{T}_\sigma\rangle+\nabla\cdot\sum_{j=1}^{j=N}(c_p)_j\langle\tilde{\rho}_j\vec{v}_j\tilde{T}_\sigma\rangle$$

$$=\nabla\cdot\left\{k_\sigma\left[\nabla\left(\varepsilon_\sigma\langle T_\sigma\rangle^\sigma\right)+\frac{1}{\mathcal{V}}\int_{A_{\sigma\gamma}}T_\sigma\vec{n}_{\sigma\gamma}dA+\frac{1}{\mathcal{V}}\int_{A_{\sigma\beta}}T_\sigma\vec{n}_{\sigma\beta}dA\right]\right\}$$

$$-\frac{1}{\mathcal{V}}\int_{A_{\sigma\gamma}}\vec{q}_\sigma\cdot\vec{n}_{\sigma\gamma}dA-\frac{1}{\mathcal{V}}\int_{A_{\sigma\beta}}\vec{q}_\sigma\cdot\vec{n}_{\sigma\beta}dA \tag{2.114}$$

This completes the continuity and thermal energy volume averaged equations for all three phases. The various continuity equations are given in several forms, depending on whether we want to include the solid velocity, and whether we just want to use the continuity equation for the liquid component only, since it is the only species which is transferring between the three phases.

3. Total Thermal Energy Equation

The three phases are assumed to be in local thermal equilibrium so that:

$$\langle T_\sigma \rangle^\sigma = \langle T_\beta \rangle^\beta = \langle T_\gamma \rangle^\gamma \tag{3.1}$$

$$\langle T \rangle \equiv \varepsilon_\sigma \langle T_\sigma \rangle^\sigma + \varepsilon_\beta \langle T_\beta \rangle^\beta + \varepsilon_\gamma \langle T_\gamma \rangle^\gamma = \langle T_\sigma \rangle^\sigma = \langle T_\beta \rangle^\beta = \langle T_\gamma \rangle^\gamma \tag{3.2}$$

We can now write the total thermal energy equation by adding together the thermal energy equations for each phase, and using the local thermal equilibrium relations given above. This equation is identical to Whitaker's, except for the addition of extra terms due to the solid-gas and solid-liquid phase interface velocities, which are no longer zero. The equation is also written so positive flux terms imply liquid evaporating into the gas phase, rather than condensing.

$$\left[\varepsilon_\sigma \left\{ \sum_{j=1}^{j=N} \langle \rho_j \rangle (c_p)_j \right\} + \varepsilon_\beta \rho_\beta (c_p)_\beta + \varepsilon_\gamma \left\{ \sum_{i=1}^{i=N} \langle \rho_i \rangle (c_p)_i \right\} \right] \frac{\partial \langle T \rangle}{\partial t}$$

$$+ \left[\sum_{j=1}^{j=N} (c_p)_j \langle \rho_j \vec{v}_j \rangle + \rho_\beta (c_p)_\beta \langle \vec{v}_\beta \rangle + \sum_{i=1}^{i=N} (c_p)_i \langle \rho_i \vec{v}_i \rangle \right] \cdot \nabla \langle T \rangle$$

$$+ \frac{1}{\mathcal{V}} \int_{A_{\sigma\gamma}} \sum_{j=1}^{j=N} \rho_j (c_p)_j \tilde{T}_\sigma (\vec{v}_\sigma - \vec{w}_1) \cdot \vec{n}_{\sigma\gamma} dA + \frac{1}{\mathcal{V}} \int_{A_{\gamma\sigma}} \sum_{i=1}^{i=N} \rho_i (c_p)_i \tilde{T}_\gamma (\vec{v}_i - \vec{w}_1) \cdot \vec{n}_{\gamma\sigma} dA$$

$$+ \frac{1}{\mathcal{V}} \int_{A_{\sigma\beta}} \sum_{j=1}^{j=N} \rho_j (c_p)_j \tilde{T}_\sigma (\vec{v}_\sigma - \vec{w}_2) \cdot \vec{n}_{\sigma\beta} dA + \frac{1}{\mathcal{V}} \int_{A_{\beta\sigma}} \rho_\beta (c_p)_\beta \tilde{T}_\beta (\vec{v}_\beta - \vec{w}_2) \cdot \vec{n}_{\beta\sigma} dA$$

$$+ \frac{1}{\mathcal{V}} \int_{A_{\beta\gamma}} \rho_\beta (c_p)_\beta \tilde{T}_\beta (\vec{v}_\beta - \vec{w}) \cdot \vec{n}_{\beta\gamma} dA + \frac{1}{\mathcal{V}} \int_{A_{\gamma\beta}} \sum_{i=1}^{i=N} \rho_i (c_p)_i \tilde{T}_\gamma (\vec{v}_i - \vec{w}) \cdot \vec{n}_{\gamma\beta} dA$$

$$= \nabla \cdot \left\{ \begin{array}{l} \nabla \left[\left(k_\sigma \varepsilon_\sigma + k_\beta \varepsilon_\beta + k_\gamma \varepsilon_\gamma \right) \langle T \rangle \right] \\ + \left(k_\sigma - k_\beta \right) \frac{1}{\mathcal{V}} \int_{A_{\sigma\beta}} T_\sigma \vec{n}_{\sigma\beta} dA \\ + \left(k_\beta - k_\gamma \right) \frac{1}{\mathcal{V}} \int_{A_{\beta\gamma}} T_\beta \vec{n}_{\beta\gamma} dA \\ + \left(k_\sigma - k_\gamma \right) \frac{1}{\mathcal{V}} \int_{A_{\sigma\gamma}} T_\gamma \vec{n}_{\sigma\gamma} dA \end{array} \right\} - \frac{1}{\mathcal{V}} \int_{A_{\sigma\beta}} \vec{q}_\sigma \cdot \vec{n}_{\sigma\beta} dA - \frac{1}{\mathcal{V}} \int_{A_{\beta\gamma}} \vec{q}_\sigma \cdot \vec{n}_{\beta\gamma} dA + \frac{1}{\mathcal{V}} \int_{A_{\gamma\sigma}} \vec{q}_\gamma \cdot \vec{n}_{\sigma\gamma} dA \tag{3.3}$$

Whitaker defines a spatial average density:

$$\langle \rho \rangle = \varepsilon_\sigma \sum_{j=1}^{j=N} \langle \rho_j \rangle^\sigma + \varepsilon_\beta \langle \rho_\beta \rangle^\beta + \varepsilon_\gamma \sum_{i=1}^{i=N} \langle \rho_i \rangle^\gamma \tag{3.4}$$

and a mass fraction weighted average heat capacity by:

$$C_p = \frac{\varepsilon_\sigma \sum_{j=1}^{j=N} \langle \rho_j \rangle^\sigma (c_p)_j + \varepsilon_\beta \rho_\beta (c_p)_\beta + \varepsilon_\gamma \sum_{i=1}^{i=N} \langle \rho_i \rangle^\gamma (c_p)_i}{\langle \rho \rangle} \tag{3.5}$$

This allows the first term in the thermal energy equation to be written as:

$$\left[\varepsilon_\sigma \left\{ \sum_{j=1}^{j=N} \langle \rho_j \rangle (c_p)_j \right\} + \varepsilon_\beta \rho_\beta (c_p)_\beta + \varepsilon_\gamma \left\{ \sum_{i=1}^{i=N} \langle \rho_i \rangle (c_p)_i \right\} \right] \frac{\partial \langle T \rangle}{\partial t} = \langle \rho \rangle C_p \frac{\partial \langle T \rangle}{\partial t} \tag{3.6}$$

We must now consider the interphase flux terms in the total thermal energy equation. In Whitaker's derivation, he only had one interphase flux term to consider, that of the exchange of mass between the liquid and the gas. We now have two more interphase fluxes to consider: that between the liquid and the solid, and that between the gas and the solid.

We first follow his derivation for the liquid-gas interface, and then apply it to the other two interfaces.

The jump boundary condition for the liquid-gas interface was shown previously to be:

$$\rho_\beta h_\beta (\vec{v}_\beta - \vec{w}) \cdot \vec{n}_{\beta\gamma} + \rho_\gamma h_\gamma (\vec{v}_\gamma - \vec{w}) \cdot \vec{n}_{\gamma\beta} = -\left\{ \vec{q}_\beta \cdot \vec{n}_{\beta\gamma} + \left[\vec{q}_\gamma + \sum_{i=1}^{i=N} \rho_i \vec{u}_i \bar{h}_i \right] \cdot \vec{n}_{\gamma\beta} \right\} \tag{3.7}$$

and this may be rewritten as:

$$\rho_\beta h_\beta (\vec{v}_\beta - \vec{w}) \cdot \vec{n}_{\beta\gamma} + \sum_{i=1}^{i=N} \rho_i \bar{h}_i (\vec{v}_i - \vec{w}) \cdot \vec{n}_{\gamma\beta} = -(\vec{q}_\beta - \vec{q}_\gamma) \cdot \vec{n}_{\beta\gamma} \tag{3.8}$$

The jump boundary condition for the solid-gas interface was shown previously to be:

$$\rho_\sigma h_\sigma (\vec{v}_\sigma - \vec{w}_1) \cdot \vec{n}_{\sigma\gamma} + \rho_\gamma h_\gamma (\vec{v}_\gamma - \vec{w}_1) \cdot \vec{n}_{\gamma\sigma} = -\left\{ \left[\vec{q}_\sigma + \sum_{j=1}^{j=N} \rho_j \vec{u}_j \bar{h}_j \right] \cdot \vec{n}_{\sigma\gamma} + \left[\vec{q}_\gamma + \sum_{i=1}^{i=N} \rho_i \vec{u}_i \bar{h}_i \right] \cdot \vec{n}_{\gamma\sigma} \right\} \tag{3.9}$$

and this may be rewritten as:

$$\sum_{j=1}^{j=N} \rho_j \bar{h}_j (\vec{v}_j - \vec{w}_1) \cdot \vec{n}_{\sigma\gamma} + \sum_{i=1}^{i=N} \rho_i \bar{h}_i (\vec{v}_i - \vec{w}_1) \cdot \vec{n}_{\gamma\sigma} = -(\vec{q}_\sigma - \vec{q}_\gamma) \cdot \vec{n}_{\sigma\gamma} \tag{3.10}$$

The jump boundary condition for the solid-liquid interface was shown previously to be:

$$\rho_\sigma h_\sigma \left(\vec{v}_\sigma - \vec{w}_2\right) \cdot \vec{n}_{\sigma\beta} + \rho_\beta h_\beta \left(\vec{v}_\beta - \vec{w}_2\right) \cdot \vec{n}_{\beta\sigma} = -\left\{ \vec{q}_\beta \cdot \vec{n}_{\beta\sigma} + \left[\vec{q}_\sigma + \sum_{j=1}^{j=N} \rho_j \vec{u}_j \vec{h}_j \right] \cdot \vec{n}_{\sigma\beta} \right\} \tag{3.11}$$

This may be rewritten as:

$$\sum_{j=1}^{j=N} \rho_j \vec{h}_j \left(\vec{v}_j - \vec{w}_2\right) \cdot \vec{n}_{\sigma\beta} + \rho_\beta h_\beta \left(\vec{v}_\beta - \vec{w}_2\right) \cdot \vec{n}_{\beta\sigma} = -\left(\vec{q}_\sigma - \vec{q}_\beta\right) \cdot \vec{n}_{\sigma\beta} \tag{3.12}$$

Using these results, we may write the interphase flux terms in the total thermal energy equation as:

$$-\frac{1}{\mathcal{V}} \int_{A_{\sigma\beta}} \left(\vec{q}_\sigma - \vec{q}_\beta\right) \cdot \vec{n}_{\sigma\beta} dA - \frac{1}{\mathcal{V}} \int_{A_{\beta\gamma}} \left(\vec{q}_\beta - \vec{q}_\gamma\right) \cdot \vec{n}_{\beta\gamma} dA - \frac{1}{\mathcal{V}} \int_{A_{\gamma\sigma}} \left(\vec{q}_\sigma - \vec{q}_\gamma\right) \cdot \vec{n}_{\sigma\gamma} dA$$

$$= +\frac{1}{\mathcal{V}} \int_{A_{\sigma\beta}} \left[\sum_{j=1}^{j=N} \rho_j \vec{h}_j \left(\vec{v}_j - \vec{w}_2\right) \cdot \vec{n}_{\sigma\beta} + \rho_\beta h_\beta \left(\vec{v}_\beta - \vec{w}_2\right) \cdot \vec{n}_{\beta\sigma} \right] dA$$

$$+\frac{1}{\mathcal{V}} \int_{A_{\beta\gamma}} \left[\rho_\beta h_\beta \left(\vec{v}_\beta - \vec{w}\right) \cdot \vec{n}_{\beta\gamma} + \sum_{i=1}^{i=N} \rho_i \vec{h}_i \left(\vec{v}_i - \vec{w}\right) \cdot \vec{n}_{\gamma\beta} \right] dA$$

$$+\frac{1}{\mathcal{V}} \int_{A_{\sigma\gamma}} \left[\sum_{j=1}^{j=N} \rho_j \vec{h}_j \left(\vec{v}_j - \vec{w}_1\right) \cdot \vec{n}_{\sigma\gamma} + \sum_{i=1}^{i=N} \rho_i \vec{h}_i \left(\vec{v}_i - \vec{w}_1\right) \cdot \vec{n}_{\gamma\sigma} \right] dA \tag{3.13}$$

The total thermal energy equation is now written as:

$$\langle\rho\rangle C_p \frac{\partial\langle T\rangle}{\partial t} + \left[\sum_{j=1}^{j=N}(c_p)_j\langle\rho_j\vec{v}_j\rangle + \rho_\beta(c_p)_\beta\langle\vec{v}_\beta\rangle + \sum_{i=1}^{i=N}(c_p)_i\langle\rho_i\vec{v}_i\rangle\right]\cdot\nabla\langle T\rangle$$

$$-\frac{1}{\mathcal{V}}\int_{A_{\sigma\beta}}\left\{\begin{array}{l}\displaystyle\sum_{j=1}^{j=N}\rho_j\left[\overline{h}_j-(c_p)_j\tilde{T}_\sigma\right](\vec{v}_j-\vec{w}_2)\cdot\vec{n}_{\sigma\beta}\\[2mm]+\rho_\beta\left[h_\beta-(c_p)_\beta\tilde{T}_\beta\right](\vec{v}_\beta-\vec{w}_2)\cdot\vec{n}_{\beta\sigma}\end{array}\right\}dA$$

$$-\frac{1}{\mathcal{V}}\int_{A_{\beta\gamma}}\left\{\begin{array}{l}\rho_\beta\left[h_\beta-(c_p)_\beta\tilde{T}_\beta\right](\vec{v}_\beta-\vec{w})\cdot\vec{n}_{\beta\gamma}\\[2mm]+\displaystyle\sum_{i=1}^{i=N}\rho_i\left[\overline{h}_i-(c_p)_i\tilde{T}_\gamma\right](\vec{v}_i-\vec{w})\cdot\vec{n}_{\gamma\beta}\end{array}\right\}dA$$

$$-\frac{1}{\mathcal{V}}\int_{A_{\sigma\gamma}}\left\{\begin{array}{l}\displaystyle\sum_{j=1}^{j=N}\rho_j\left[\overline{h}_j-(c_p)_j\tilde{T}_\sigma\right](\vec{v}_j-\vec{w}_1)\cdot\vec{n}_{\sigma\gamma}\\[2mm]+\displaystyle\sum_{i=1}^{i=N}\rho_i\left[\overline{h}_i-(c_p)_i\tilde{T}_\gamma\right](\vec{v}_i-\vec{w}_1)\cdot\vec{n}_{\gamma\sigma}\end{array}\right\}dA$$

$$=\nabla\cdot\left\{\begin{array}{l}\nabla\left[\left(k_\sigma\varepsilon_\sigma+k_\beta\varepsilon_\beta+k_\gamma\varepsilon_\gamma\right)\langle T\rangle\right]\\[2mm]+\left(k_\sigma-k_\beta\right)\dfrac{1}{\mathcal{V}}\int_{A_{\sigma\beta}}T_\sigma\vec{n}_{\sigma\beta}dA\\[2mm]+\left(k_\beta-k_\gamma\right)\dfrac{1}{\mathcal{V}}\int_{A_{\beta\gamma}}T_\beta\vec{n}_{\beta\gamma}dA\\[2mm]+\left(k_\sigma-k_\gamma\right)\dfrac{1}{\mathcal{V}}\int_{A_{\sigma\gamma}}T_\gamma\vec{n}_{\sigma\gamma}dA\end{array}\right\}$$

(3.14)

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Next, we can begin to express the phase interface velocities in terms of enthalpies of vaporization, sorption, and desorption.

The enthalpies for each phase were defined previously as:

$$\bar{h}_j = h_j^{\circ} + (c_p)_j (T_\sigma - T_\sigma^{\circ})$$ (3.15)

$$h_\beta = h_\beta^{\circ} + (c_p)_\beta (T_\beta - T_\beta^{\circ})$$ (3.16)

$$\bar{h}_i = h_i^{\circ} + (c_p)_i (T_\gamma - T_\gamma^{\circ})$$ (3.17)

We also know that the intrinsic phase average temperatures, temperature dispersion, and overall average temperatures are related by:

$$\tilde{T}_\sigma = \langle T_\sigma \rangle^{\sigma} - T_\sigma$$ (3.18)

$$\tilde{T}_\beta = \langle T_\beta \rangle^{\beta} - T_\beta$$ (3.19)

$$\tilde{T}_\gamma = \langle T_\gamma \rangle^{\gamma} - T_\gamma$$ (3.20)

$$\langle T_\sigma \rangle^{\sigma} = \langle T_\beta \rangle^{\beta} = \langle T_\gamma \rangle^{\gamma} = \langle T \rangle$$ (3.21

We may use these relations to rewrite the integrands inside the volume integrals on the left hand side of the total thermal energy equation. Whitaker gives the result for the liquid-gas interface as:

$$-\frac{1}{\mathcal{V}} \int_{A_{\beta\gamma}} \left\{ \rho_\beta \left[h_\beta - (c_p)_\beta \tilde{T}_\beta \right] (\vec{v}_\beta - \vec{w}) \cdot \vec{n}_{\beta\gamma} + \sum_{i=1}^{i=N} \rho_i \left[\bar{h}_i - (c_p)_i \tilde{T}_\gamma \right] (\vec{v}_i - \vec{w}) \cdot \vec{n}_{\gamma\beta} \right\} dA$$

$$= -\frac{1}{\mathcal{V}} \int_{A_{\beta\gamma}} \left\{ \begin{array}{l} \left[h_\beta^{\circ} - (c_p)_\beta \left(\langle T_\beta \rangle^{\beta} - T_\beta^{\circ} \right) \right] \rho_\beta (\vec{v}_\beta - \vec{w}) \cdot \vec{n}_{\beta\gamma} \\ + \sum_{i=1}^{i=N} \left[h_i^{\circ} - (c_p)_i \left(\langle T_\gamma \rangle^{\gamma} - T_\gamma^{\circ} \right) \right] \rho_i (\vec{v}_i - \vec{w}) \cdot \vec{n}_{\gamma\beta} \end{array} \right\} dA$$ (3.22)

From the species jump conditions:

$$\rho_i (\vec{v}_i - \vec{w}) \cdot \vec{n}_{\gamma\beta} + \rho_\beta (\vec{v}_\beta - \vec{w}) \cdot \vec{n}_{\beta\gamma} = 0 \quad , \quad i = 1$$ (3.23)

$$\rho_i (\vec{v}_i - \vec{w}) \cdot \vec{n}_{\gamma\beta} = 0 \quad , \quad i = 2, 3, \ldots$$ (3.24)

where the subscript 1 refers to the component (water) which is actually crossing the phase boundary as it goes from a liquid to a vapor.

From the species jump conditions we may also write:

$$\rho_1\left(\vec{v}_1 - \vec{w}_2\right)\cdot \vec{n}_{\sigma\beta} = -\rho_\beta\left(\vec{v}_\beta - \vec{w}_2\right)\cdot \vec{n}_{\beta\sigma} \qquad (3.25)$$

We may rewrite the integral as:

$$-\frac{1}{\mathcal{V}}\int_{A_{\beta\gamma}}\left\{\begin{array}{l}\left[h_\beta^\circ - \left(c_p\right)_\beta\left(\langle T\rangle - T_\beta^\circ\right)\right]\rho_\beta\left(\vec{v}_\beta - \vec{w}\right)\cdot \vec{n}_{\beta\gamma} \\ +\left[h_{g1}^\circ - \left(c_p\right)_1\left(\langle T\rangle - T_\gamma^\circ\right)\right]\rho_1\left(\vec{v}_1 - \vec{w}\right)\cdot \vec{n}_{\gamma\beta}\end{array}\right\}dA$$

$$=-\frac{1}{\mathcal{V}}\int_{A_{\beta\gamma}}\left\{\begin{array}{l}\left[h_\beta^\circ - \left(c_p\right)_\beta\left(\langle T\rangle - T_\beta^\circ\right)\right]\rho_\beta\left(\vec{v}_\beta - \vec{w}\right)\cdot \vec{n}_{\beta\gamma} \\ -\left[h_{g1}^\circ - \left(c_p\right)_1\left(\langle T\rangle - T_\gamma^\circ\right)\right]\rho_1\left(\vec{v}_1 - \vec{w}\right)\cdot \vec{n}_{\beta\gamma}\end{array}\right\}dA$$

$$=\left\{\begin{array}{l}\left[h_{g1}^\circ - h_\beta^\circ + \left(c_p\right)_1\left(\langle T\rangle - T_\gamma^\circ\right)\right] \\ -\left(c_p\right)_\beta\left(\langle T\rangle - T_\beta^\circ\right)\end{array}\right\}\frac{1}{\mathcal{V}}\int_{A_{\beta\gamma}}\rho_\beta\left(\vec{v}_\beta - \vec{w}\right)\cdot \vec{n}_{\beta\gamma}dA \qquad (3.26)$$

We may use the following definitions:

$$\Delta h_{vap}\ \ (\text{at temperature } \langle T\rangle) = \left\{\left[h_{g1}^\circ - h_\beta^\circ + \left(c_p\right)_1\left(\langle T\rangle - T_\gamma^\circ\right) - \left(c_p\right)_\beta\left(\langle T\rangle - T_\beta^\circ\right)\right]\right\} \qquad (3.27)$$

$$\langle \dot{m}_{lv}\rangle = \frac{1}{\mathcal{V}}\int_{A_{\beta\gamma}}\rho_\beta\left(\vec{v}_\beta - \vec{w}\right)\cdot \vec{n}_{\beta\gamma}dA \qquad (3.28)$$

to rewrite the integral as:

$$-\frac{1}{\mathcal{V}}\int_{A_{\beta\gamma}}\left\{\begin{array}{l}\rho_\beta\left[h_\beta - \left(c_p\right)_\beta \tilde{T}_\beta\right]\left(\vec{v}_\beta - \vec{w}\right)\cdot \vec{n}_{\beta\gamma} + \\ \sum_{i=1}^{i=N}\rho_i\left[\bar{h}_i - \left(c_p\right)_i \tilde{T}_\gamma\right]\left(\vec{v}_i - \vec{w}\right)\cdot \vec{n}_{\gamma\beta}\end{array}\right\}dA = \Delta h_{vap}\langle \dot{m}_{lv}\rangle \qquad (3.29)$$

The corresponding terms for the phase interface between the solid and the liquid are identical, except that we no longer use the quantity Δh_{vap}, but instead use the differential enthalpy of sorption[7], which we will give the notation Q_l. The differential heat of sorption is the heat evolved when one gram of water is absorbed by an infinite mass of the solid, when that solid is at a particular equilibrated moisture content. This is very similar to the heat of solution or heat of mixing that occurs when two liquid components are mixed. For textile fibers there is a definite relationship between the equilibrium values of the differential heat of sorption and the water content of the fibers, and we can use those relationships in our thermodynamic equations which will be discussed in a later section.

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The solid-liquid interface integral term is thus given as:

$$-\frac{1}{\mathcal{V}}\int_{A_{\sigma\beta}}\left\{\begin{array}{l}\rho_\beta\left[h_\beta-(c_p)_\beta\tilde{T}_\beta\right](\vec{v}_\beta-\vec{w}_2)\cdot\vec{n}_{\beta\sigma}\\[2mm]+\sum_{j=1}^{j=N}\rho_j\left[\bar{h}_j-(c_p)_j\tilde{T}_\sigma\right](\vec{v}_j-\vec{w}_2)\cdot\vec{n}_{\sigma\beta}\end{array}\right\}dA \tag{3.30}$$

From the species jump conditions we may also write:

$$\rho_1(\vec{v}_1-\vec{w}_2)\cdot\vec{n}_{\sigma\beta}=-\rho_\beta(\vec{v}_\beta-\vec{w}_2)\cdot\vec{n}_{\beta\sigma} \tag{3.31}$$

We may rewrite the integral as:

$$-\frac{1}{\mathcal{V}}\int_{A_{\sigma\beta}}\left\{\begin{array}{l}\left[h_\beta^\circ-(c_p)_\beta(\langle T\rangle-T_\beta^\circ)\right]\rho_\beta(\vec{v}_\beta-\vec{w}_2)\cdot\vec{n}_{\beta\sigma}\\[2mm]+\left[h_{s1}^\circ-(c_p)_1(\langle T\rangle-T_\sigma^\circ)\right]\rho_1(\vec{v}_1-\vec{w}_2)\cdot\vec{n}_{\sigma\beta}\end{array}\right\}dA$$

$$=-\frac{1}{\mathcal{V}}\int_{A_{\sigma\beta}}\left\{\begin{array}{l}\left[h_{s1}^\circ-(c_p)_1(\langle T\rangle-T_\sigma^\circ)\right]\rho_1(\vec{v}_1-\vec{w}_2)\cdot\vec{n}_{\sigma\beta}\\[2mm]-\left[h_\beta^\circ-(c_p)_\beta(\langle T\rangle-T_\beta^\circ)\right]\rho_\beta(\vec{v}_\beta-\vec{w}_2)\cdot\vec{n}_{\sigma\beta}\end{array}\right\}dA$$

$$=\left\{\left[h_{s1}^\circ-h_\beta^\circ+(c_p)_{s1}(\langle T\rangle-T_\sigma^\circ)-(c_p)_\beta(\langle T\rangle-T_\beta^\circ)\right]\right\}\frac{1}{\mathcal{V}}\int_{A_{\sigma\beta}}\rho_\beta(\vec{v}_\beta-\vec{w}_2)\cdot\vec{n}_{\sigma\beta}dA \tag{3.32}$$

We may use the following definitions:

$$Q_1\ \text{(at temperature }\langle T\rangle)=\left[h_{s1}^\circ-h_\beta^\circ+(c_p)_1(\langle T\rangle-T_\sigma^\circ)-(c_p)_\beta(\langle T\rangle-T_\beta^\circ)\right] \tag{3.33}$$

$$\langle\dot{m}_{sl}\rangle=\frac{1}{\mathcal{V}}\int_{A_{\sigma\beta}}\rho_\sigma(\vec{v}_\sigma-\vec{w}_2)\cdot\vec{n}_{\sigma\beta}dA \tag{3.34}$$

to rewrite the original integral as:

$$-\frac{1}{\mathcal{V}}\int_{A_{\sigma\beta}}\left\{\sum_{j=1}^{j=N}\rho_j\left[\bar{h}_j-(c_p)_j\tilde{T}_\sigma\right](\vec{v}_j-\vec{w}_2)\cdot\vec{n}_{\sigma\beta}+\rho_\beta\left[h_\beta-(c_p)_\beta\tilde{T}_\beta\right](\vec{v}_\beta-\vec{w}_2)\cdot\vec{n}_{\beta\sigma}\right\}dA=Q_1\langle\dot{m}_{sl}\rangle \tag{3.35}$$

For the gas-solid interface, the heat of desorption for the vapor is equal to the energy required to desorb the liquid plus the enthalpy of vaporization required to evaporate the liquid:

$$Q_v = Q_l + \Delta h_{vap} \tag{3.36}$$

The derivation is exactly the same as for the other two interfaces, where the only component crossing the phase interface is component 1 (water) and we may write the integral as:

$$-\frac{1}{\mathcal{V}}\int_{A_{\sigma\gamma}}\left\{\sum_{j=1}^{j=N}\rho_j\left[\tilde{h}_j-(c_P)_j\tilde{T}_\sigma\right](\vec{v}_j-\vec{w}_1)\cdot\vec{n}_{\sigma\gamma}+\sum_{i=1}^{i=N}\rho_i\left[\tilde{h}_i-(c_P)_i\tilde{T}_\gamma\right](\vec{v}_i-\vec{w}_1)\cdot\vec{n}_{\gamma\sigma}\right\}dA$$

$$=\left(Q_l+\Delta h_{vap}\right)\left\langle\dot{m}_{sv}\right\rangle \tag{3.37}$$

For these equations $\left\langle\dot{m}_{sl}\right\rangle$ is the mass flux desorbing from the solid to the liquid phase, $\left\langle\dot{m}_{sv}\right\rangle$ is the mass flux desorbing from the solid into the gas phase, and $\left\langle\dot{m}_{lv}\right\rangle$ is the mass flux evaporating from the liquid phase to the gas phase.

The total thermal energy equation now becomes:

$$\langle\rho\rangle C_P\frac{\partial\langle T\rangle}{\partial t}+\left[\sum_{j=1}^{j=N}(c_P)_j\left\langle\rho_j\vec{v}_j\right\rangle+\rho_\beta(c_P)_\beta\left\langle\vec{v}_\beta\right\rangle+\sum_{i=1}^{i=N}(c_P)_i\left\langle\rho_i\vec{v}_i\right\rangle\right]\cdot\nabla\langle T\rangle$$

$$+\Delta h_{vap}\left\langle\dot{m}_{lv}\right\rangle+Q_l\left\langle\dot{m}_{sl}\right\rangle+\left(Q_l+\Delta h_{vap}\right)\left\langle\dot{m}_{sv}\right\rangle$$

$$=\nabla\cdot\left\{\begin{array}{l}\nabla\left[\left(k_\sigma\varepsilon_\sigma+k_\beta\varepsilon_\beta+k_\gamma\varepsilon_\gamma\right)\langle T\rangle\right]\\[2mm]+\left(k_\sigma-k_\beta\right)\dfrac{1}{\mathcal{V}}\int_{A_{\sigma\beta}}T_\sigma\vec{n}_{\sigma\beta}dA\\[2mm]+\left(k_\beta-k_\gamma\right)\dfrac{1}{\mathcal{V}}\int_{A_{\beta\gamma}}T_\beta\vec{n}_{\beta\gamma}dA\\[2mm]+\left(k_\sigma-k_\gamma\right)\dfrac{1}{\mathcal{V}}\int_{A_{\sigma\gamma}}T_\gamma\vec{n}_{\sigma\gamma}dA\end{array}\right\} \tag{3.38}$$

We may simplify the total thermal energy equation based on an effective thermal conductivity, and write our total thermal energy equation in a much shorter form as:

$$\langle \rho \rangle C_p \frac{\partial \langle T \rangle}{\partial t} + \left[\sum_{j=1}^{j=N} (c_p)_j \langle \rho_j \bar{v}_j \rangle + \rho_\beta (c_p)_\beta \langle \bar{v}_\beta \rangle + \sum_{i=1}^{i=N} (c_p)_i \langle \rho_i \bar{v}_i \rangle \right] \cdot \nabla \langle T \rangle$$

$$+ \Delta h_{vap} \langle \dot{m}_{lv} \rangle + Q_l \langle \dot{m}_{sl} \rangle + (Q_l + \Delta h_{vap}) \langle \dot{m}_{sv} \rangle$$

$$= \nabla \cdot \left(K_{eff}^T \cdot \nabla \langle T \rangle \right) \tag{3.39}$$

The effective thermal conductivity can be expressed in a variety of ways as described by Whitaker, depending on the assumptions you choose to make about the isotropy of the porous medium, the importance of the dispersion terms, etc. The effective thermal conductivity is also an appropriate place to include radiative heat transfer, and one could add an apparent radiative component of thermal conductivity to the effective thermal conductivity to account for radiation heat transfer.

4. Thermodynamic Relations

The gas phase is assumed to be ideal, which gives the intrinsic phase partial pressures of the gas phase as:

$$\langle p_i \rangle^\gamma = \langle \rho_i \rangle^\gamma R_i \langle T \rangle \quad i = 1, 2, \ldots \tag{4.1}$$

We also have the relations for the gas phase, where for our case component 1 is water, and component 2 is air:

$$\langle \rho_\gamma \rangle^\gamma = \langle \rho_1 \rangle^\gamma + \langle \rho_2 \rangle^\gamma \tag{4.2}$$

$$\langle p_\gamma \rangle^\gamma = \langle p_1 \rangle^\gamma + \langle p_2 \rangle^\gamma \tag{4.3}$$

We must also connect the differential heat of sorption, Q_1, with the concentration of water in the solid phase. An example of a general form for Q_1, (in Joules/gram) can be expressed as a function of the relative humidity[8]:

$$Q_l \ (\text{J} / \text{g}) = 195(1-\phi)\left(\frac{1}{(0.2 + \phi)} + \frac{1}{(1.05 - \phi)}\right) \quad, \quad \text{where relative humidity} \quad \phi = \frac{p}{p_s} = \frac{\langle p_1 \rangle^\gamma}{p_s} \tag{4.4}$$
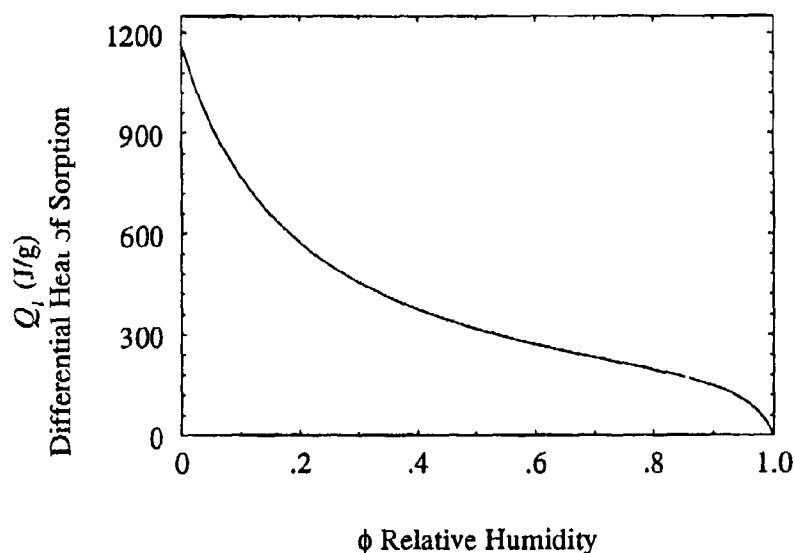
Figure 4. Generic differential heat of sorption for textile fibers (sorption hysteresis neglected).

We must connect the differential heat of sorption with the actual equilibrium water content in the solid phase. For the two component mixture of solid (component 2) plus bound water (component 1) in the solid phase, the density of the solid phase is given by:

$$\langle \rho_\sigma \rangle^\sigma = \langle \rho_1 \rangle^\sigma + \langle \rho_2 \rangle^\sigma \tag{4.5}$$

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We could make the assumption that mass transport in the textile fiber portion is so rapid that the fiber is always in equilibrium with the partial pressure of the gas phase, or is saturated if any liquid phase is present. This would eliminate the need to account for the transport through the solid phase at all. There are a variety of sorption isotherm relationships we could use, including the experimentally-determined relationships for a specific fiber type, but a convenient one is given by[8]:

$$\text{Regain } (R) = R_f(0.55\phi)\left[\frac{1}{(0.25+\phi)}+\frac{1}{(1.25-\phi)}\right] \tag{4.6}$$

R_f is the standard textile measurement of grams of water absorbed per 100 grams of fiber, measured at 65% relative humidity. We may rewrite this in terms of the intrinsic phase averages for our two phases as:

$$R = \frac{\langle\rho_1\rangle^\sigma}{100\langle\rho_2\rangle^\sigma} = R_f\left(55\frac{\langle p_1\rangle^\gamma}{p_s}\right)\left[\frac{1}{\left(0.25+\frac{\langle p_1\rangle^\gamma}{p_s}\right)}+\frac{1}{\left(1.25-\frac{\langle p_1\rangle^\gamma}{p_s}\right)}\right] \tag{4.7}$$

If we don't want to make the assumption that the solid phase is always in equilibrium, we may use relations available between the rate of change of concentration of the solid phase and the relative humidity of the gas phase, an example of which is given by Norden and David[9] .

We may also write the vapor pressure-temperature relation for the vaporizing β phase, which Whitaker gives for porous media as:

$$\langle p_1\rangle^\gamma = p_1^\circ \exp\left\{-\left[\left(\frac{2\sigma_{\beta\gamma}}{r\rho_\beta R_1\langle T\rangle}\right)+\frac{\Delta h_{vap}}{R_1}\left(\frac{1}{\langle T\rangle}-\frac{1}{T_\circ}\right)\right]\right\} \tag{4.8}$$

This relation gives the reduction or increase in vapor pressure from a curved liquid surface resulting from a liquid droplet influenced by the surface interaction between the solid and the liquid, usually in a very small capillary.

In many cases, the Clausis-Clapeyron equation will be sufficiently accurate for the vaporizing species, and the gas phase vapor pressure may be found from:

$$\langle p_1\rangle^\gamma = p_1^\circ \exp\left\{-\left[\frac{\Delta h_{vap}}{R_1}\left(\frac{1}{\langle T\rangle}-\frac{1}{T_\circ}\right)\right]\right\} \tag{4.9}$$

This vapor pressure-temperature relation is only good if we have the liquid phase present in the averaging volume. We may also have the situation where we only have the solid phase, containing adsorbed water, and the gas phase. To get the vapor pressure in the gas phase in this situation, we will use the sorption isotherm, and assume that the gas phase is in equilibrium with the sorbed water content of the solid phase.

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We can use any isotherm relation where we have the solid water concentration as a function of relative humidity. The equation given previously is one example:

$$\frac{\langle \rho_1 \rangle^\sigma}{\langle \rho_2 \rangle^\sigma} = \frac{\varepsilon_{\sigma l}\rho_l}{(1-\varepsilon_{\sigma l})\rho_s} = R_f \left(0.55 \frac{\langle p_1 \rangle^\gamma}{p_s} \right) \left[\frac{1}{\left(0.25 + \dfrac{\langle p_1 \rangle^\gamma}{p_s} \right)} + \frac{1}{\left(1.25 - \dfrac{\langle p_1 \rangle^\gamma}{p_s} \right)} \right] \tag{4.10}$$

From a curve-fit, or some kind of equation solver, we find that the partial vapor pressure can be given as a function of the volume fraction of water in the solid phase:

$$\langle p_1 \rangle^\gamma = f(p_s, \rho_l, \rho_s, \varepsilon_{\sigma l}) \quad \text{at the temperature } \langle T \rangle, \text{ only } \varepsilon_{\sigma l} \text{ is unknown.} \tag{4.11}$$

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5. Mass Transport in the Gas Phase

The volume average form of the gas phase continuity equation was found to be:

$$\frac{\partial}{\partial t}\left(\varepsilon_\gamma \langle \rho_\gamma \rangle^\gamma\right) + \nabla \cdot \left(\langle \rho_\gamma \rangle^\gamma \langle \vec{v}_\gamma \rangle\right) + \frac{1}{\mathcal{V}}\int_{A_{\gamma\beta}} \rho_\gamma\left(\vec{v}_\gamma - \vec{w}\right)\cdot \vec{n}_{\gamma\beta}\,dA + \frac{1}{\mathcal{V}}\int_{A_{\gamma\sigma}} \rho_\gamma\left(\vec{v}_\gamma - \vec{w}_1\right)\cdot \vec{n}_{\gamma\sigma}\,dA = 0 \quad (5.1)$$

and the species continuity equation was given as:

$$\frac{\partial}{\partial t}\left(\varepsilon_\gamma \langle \rho_1 \rangle^\gamma\right) + \nabla \cdot \left(\langle \rho_1 \rangle^\gamma \langle \vec{v}_1 \rangle\right) + \frac{1}{\mathcal{V}}\int_{A_{\gamma\beta}} \rho_1\left(\vec{v}_1 - \vec{w}\right)\cdot \vec{n}_{\gamma\beta}\,dA = \nabla \cdot \left\{\langle \rho_\gamma \rangle^\gamma \mathcal{D}\nabla\left(\frac{\langle \rho_i \rangle^\gamma}{\langle \rho_\gamma \rangle^\gamma}\right)\right\} \quad (5.2)$$

where the dispersion and source terms were dropped from the equation.

If we use the definition of the mass flux from one phase to another as:

$$\langle \dot{m}_{lv} \rangle = \frac{1}{\mathcal{V}}\int_{A_{\beta\gamma}} \rho_\beta\left(\vec{v}_\beta - \vec{w}\right)\cdot \vec{n}_{\beta\gamma}\,dA \quad (5.3)$$

or

$$\langle \dot{m}_{lv} \rangle = -\frac{1}{\mathcal{V}}\int_{A_{\beta\gamma}} \rho_\gamma\left(\vec{v}_\gamma - \vec{w}\right)\cdot \vec{n}_{\gamma\beta}\,dA \quad , \quad (5.4)$$

with the same form for the mass flux from the solid to the gas phase, the gas phase continuity equation may be rewritten as:

$$\frac{\partial}{\partial t}\left(\varepsilon_\gamma \langle \rho_\gamma \rangle^\gamma\right) + \nabla \cdot \left(\langle \rho_\gamma \rangle^\gamma \langle \vec{v}_\gamma \rangle\right) = \langle \dot{m}_{lv} \rangle + \langle \dot{m}_{sv} \rangle \quad (5.5)$$

For the two species (1--water, and 2--air), the species continuity equations are written (again dropping the source and dispersion terms) as:

$$\frac{\partial}{\partial t}\left(\varepsilon_\gamma \langle \rho_1 \rangle^\gamma\right) + \nabla \cdot \left(\langle \rho_1 \rangle^\gamma \langle \vec{v}_\gamma \rangle\right) - \langle \dot{m}_{lv} \rangle - \langle \dot{m}_{sv} \rangle = \nabla \cdot \left\{\langle \rho_\gamma \rangle^\gamma \mathcal{D}\nabla\left(\frac{\langle \rho_1 \rangle^\gamma}{\langle \rho_\gamma \rangle^\gamma}\right)\right\} \quad (5.6)$$

$$\frac{\partial}{\partial t}\left(\varepsilon_\gamma \langle \rho_2 \rangle^\gamma\right) + \nabla \cdot \left(\langle \rho_2 \rangle^\gamma \langle \vec{v}_\gamma \rangle\right) = \nabla \cdot \left\{\langle \rho_\gamma \rangle^\gamma \mathcal{D}\nabla\left(\frac{\langle \rho_2 \rangle^\gamma}{\langle \rho_\gamma \rangle^\gamma}\right)\right\} \quad (5.7)$$

If we again ignore the effects of the dispersion terms in the diffusion equations derived by Whitaker, we may incorporate an effective diffusivity into the species continuity equations, which are now given as:

$$\frac{\partial}{\partial t}\left(\varepsilon_\gamma \langle \rho_1 \rangle^\gamma\right) + \nabla \cdot \left(\langle \rho_1 \rangle^\gamma \langle \bar{v}_\gamma \rangle\right) - \langle \dot{m}_{lv} \rangle - \langle \dot{m}_{sv} \rangle = \nabla \cdot \left\{ \langle \rho_\gamma \rangle^\gamma \mathcal{D}_{eff} \nabla \left(\frac{\langle \rho_1 \rangle^\gamma}{\langle \rho_\gamma \rangle^\gamma} \right) \right\} \tag{5.8}$$

$$\frac{\partial}{\partial t}\left(\varepsilon_\gamma \langle \rho_2 \rangle^\gamma\right) + \nabla \cdot \left(\langle \rho_2 \rangle^\gamma \langle \bar{v}_\gamma \rangle\right) = \nabla \cdot \left\{ \langle \rho_\gamma \rangle^\gamma \mathcal{D}_{eff} \nabla \left(\frac{\langle \rho_2 \rangle^\gamma}{\langle \rho_\gamma \rangle^\gamma} \right) \right\} \tag{5.9}$$

The effective diffusivity will be some kind of function of the gas phase volume ε; as the solid volume and the liquid volume fractions increase, there will be less space available in the gas phase for the diffusion to take place. We might try to define the effective diffusivity as:

$$D_{eff} = \frac{D_{12}\varepsilon_\gamma}{\tau} = \frac{D_a \varepsilon_\gamma}{\tau} \quad , \tag{5.10}$$

where the effective diffusivity D_{eff} is related to the diffusion coefficient of water vapor in air (D_{12} or D_a) divided by the effective tortuosity factor τ.

An example of a good relation for the binary diffusion coefficient of water vapor in air is given by Stanish[9] as:

$$D_{12} = \left(\frac{2.23}{\langle p_1 \rangle^\gamma + \langle p_2 \rangle^\gamma} \right) \left(\frac{T}{273.15} \right)^{1.75} \quad \text{(mks units)} \tag{5.11}$$

To simplify matters, one could assume the tortuosity factor to be constant, and let the variation in the gas phase volume take care of the change in the effective diffusion coefficient as the volume available for gas phase diffusion changes with solid swelling and/or liquid volume.

Another simplification is to only account for the water vapor movement, so the continuity equation would become:

$$\frac{\partial}{\partial t}\left(\varepsilon_\gamma \langle \rho_1 \rangle^\gamma\right) + \nabla \cdot \left(\langle \rho_1 \rangle^\gamma \langle \bar{v}_\gamma \rangle\right) - \langle \dot{m}_{lv} \rangle - \langle \dot{m}_{sv} \rangle = \nabla \cdot \left\{ \langle \rho_\gamma \rangle^\gamma \frac{D_{12}}{\tau} \nabla \left(\frac{\langle \rho_1 \rangle^\gamma}{\langle \rho_\gamma \rangle^\gamma} \right) \right\} \tag{5.12}$$

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6. Gas Phase Convective Transport

It is important to include forced convection through porous media since this can be an important part of the transport process of mass and energy through porous materials with high air permeability.

It is not necessary to modify any of Whitaker's derivations for the gas phase, and if we neglect gravity, we may write the gas phase velocity as:

$$\langle \vec{v}_\gamma \rangle = -\frac{1}{\mu_\gamma} K_\gamma \cdot \left\{ \varepsilon_\gamma \left[\nabla \langle p_\gamma - p_0 \rangle^\gamma \right] \right\} \tag{6.1}$$

where the permeability tensor K_γ is a transport coefficient.

There are other methods to obtain an estimate of the convective velocity of a gas flow through a porous material. It may be desirable to use one of these other relations to obtain the volume average form of the gas velocity.

For example, we could start directly with Darcy's law:

$$\nabla P + \frac{\mu}{K} \vec{v}_\gamma = 0 \tag{6.2}$$

and assume that for the dry porous material we have available the experimental measurement of the specific permeability coefficient K, and then modify it to account for the decrease in gas phase volume as the solid phase swells and/or the liquid phase accumulates. We could make the variation in K a linear function of the gas phase volume, which has been an approach used by Stanish et. al.[11]

$$K_\gamma = K_{dry}^\gamma \left(\frac{\varepsilon_\gamma}{\varepsilon_{\gamma dry}} \right) \tag{6.3}$$

This is a very simple model, and may be improved upon. In the book by Dullien[12], there are a variety of relationships for how K varies with porosity; some of those relations may be more realistic for our purposes. We could also relate the change in the permeability to the effective tortuosity function τ, which also has the same factors related to the decrease in gas phase volume, and change in geometry, that we need to account for the Darcy's law relation for convective gas flow.

7. Liquid Phase Convective Transport

Whitaker's derivation for the convection transport of the liquid phase is the one of the most complicated parts of his general theory. He accounts for the capillary liquid transport, which is greatly influenced by the geometry of the solid phase, and the changeover from a continuous to a discontinuous liquid phase. His eventual transport equation, which gives an expression for the liquid phase average velocity is quite complicated, and depends on several hard-to-obtain transport coeffients. The final equation is given as:

$$\langle \bar{v}_\beta \rangle = -\left(\frac{\varepsilon_\beta \xi K_\beta}{\mu_\beta} \right) \cdot \left[k_\varepsilon \nabla \varepsilon_\beta + k_{\langle T \rangle} \nabla \langle T \rangle - \left(\rho_\beta - \rho_\gamma \right) \right] \qquad (7.1)$$

(symbol definitions given in nomenclature table)

One advantage of Whitaker's derivation is that it is almost completely independent of the other transport equation derivations. This should mean that we may use another expression for the liquid phase velocity if we find one that is more amenable to experimental measurement and verification.

An example of an equation which is more empirical is again given by Stanish[11]. The velocity is assumed proportional to the gradient in pressure within the liquid. The pressure in the liquid phase is assumed to be the sum of the gas pressure within the averaging volume minus the capillary pressure (P_c):

$$\langle \bar{v}_\beta \rangle = -\left(\frac{k_\beta}{\mu_\beta} \right) \nabla \left(\langle p_1 \rangle^\gamma + \langle p_2 \rangle^\gamma - P_c \right) \qquad (7.2)$$

If we use a relation of this kind it is necessary to obtain an equation for the capillary pressure as a function of the fraction of non-solid volume occupied by the liquid phase, as well as a relation for the variation in the permeability coefficient as a function of liquid phase volume fraction. It is also necessary to to determine when the liquid phase becomes discontinuous so that liquid flow ceases at that point. These types of relations can be determined experimentally for materials of interest, or they may be found in the literature for quite a wide variety of materials.

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8. Summary of Modified Transport Equations

The set of modified equations which describe the coupled transfer of heat and mass through hygroscopic porous materials are summarized below.

Total thermal energy equation (8.1)

$$\langle\rho\rangle C_p \frac{\partial\langle T\rangle}{\partial t} + \begin{bmatrix} \sum_{j=1}^{j=N}(c_p)_j\langle\rho_j\vec{v}_j\rangle \\ +\rho_\beta(c_p)_\beta\langle\vec{v}_\beta\rangle \\ +\sum_{i=1}^{i=N}(c_p)_i\langle\rho_i\vec{v}_i\rangle \end{bmatrix} \cdot \nabla\langle T\rangle + \Delta h_{vap}\langle\dot{m}_{lv}\rangle + Q_l\langle\dot{m}_{sl}\rangle + (Q_l + \Delta h_{vap})\langle\dot{m}_{sv}\rangle = \nabla\cdot\left(K_{eff}^T\cdot\nabla\langle T\rangle\right)$$

Liquid phase equation of motion

$$\langle\vec{v}_\beta\rangle = -\left(\frac{k_\beta}{\mu_\beta}\right)\nabla\left(\langle p_1\rangle^\gamma + \langle p_2\rangle^\gamma - P_c\right)$$

(8.2)

Liquid phase continuity equation

$$\frac{\partial\varepsilon_\beta}{\partial t} + \nabla\cdot\langle\vec{v}_\beta\rangle + \frac{1}{\mathcal{V}}\int_{A_{\beta\gamma}}\left(\vec{v}_\beta - \vec{w}\right)\cdot\vec{n}_{\beta\gamma}dA + \frac{1}{\mathcal{V}}\int_{A_{\beta\sigma}}\left(\vec{v}_\beta - \vec{w}_2\right)\cdot\vec{n}_{\beta\sigma}dA = 0$$

(8.3)

which may be rewritten as:

$$\frac{\partial\varepsilon_\beta}{\partial t} + \nabla\cdot\langle\vec{v}_\beta\rangle + \frac{\left(\langle\dot{m}_{lv}\rangle - \langle\dot{m}_{sv}\rangle\right)}{\rho_\beta} = 0$$

(8.40

Gas phase equation of motion

$$\langle\vec{v}_\gamma\rangle = -\left(\frac{k_\gamma}{\mu_\gamma}\right)\nabla\left(\langle p_1\rangle^\gamma + \langle p_2\rangle^\gamma\right)$$

(8.5)

Gas phase continuity equation

$$\frac{\partial}{\partial t}\left(\varepsilon_\gamma\langle\rho_\gamma\rangle^\gamma\right) + \nabla\cdot\left(\langle\rho_\gamma\rangle^\gamma\langle\vec{v}_\gamma\rangle\right) = \langle\dot{m}_{lv}\rangle + \langle\dot{m}_{sv}\rangle$$

(8.6)

Gas phase diffusion equations

$$\frac{\partial}{\partial t}\left(\varepsilon_\gamma \langle \rho_1 \rangle^\gamma\right) + \nabla \cdot \left(\langle \rho_1 \rangle^\gamma \langle \bar{v}_\gamma \rangle\right) - \langle \dot{m}_{lv} \rangle - \langle \dot{m}_{sv} \rangle = \nabla \cdot \left\{ \langle \rho_\gamma \rangle^\gamma \mathcal{D}_{eff} \nabla \left(\frac{\langle \rho_1 \rangle^\gamma}{\langle \rho_\gamma \rangle^\gamma} \right) \right\} \tag{8.7}$$

$$\frac{\partial}{\partial t}\left(\varepsilon_\gamma \langle \rho_2 \rangle^\gamma\right) + \nabla \cdot \left(\langle \rho_2 \rangle^\gamma \langle \bar{v}_\gamma \rangle\right) = \nabla \cdot \left\{ \langle \rho_\gamma \rangle^\gamma \mathcal{D}_{eff} \nabla \left(\frac{\langle \rho_2 \rangle^\gamma}{\langle \rho_\gamma \rangle^\gamma} \right) \right\} \tag{8.8}$$

Solid phase density relations

$$\langle \rho_\sigma \rangle^\sigma = \langle \rho_1 \rangle^\sigma + \langle \rho_2 \rangle^\sigma \tag{8.9}$$

$$\rho_1 = \varepsilon_{\sigma L} \rho_L \tag{8.10}$$

$$\rho_2 = (1 - \varepsilon_{\sigma L}) \rho_S \tag{8.11}$$

$$\varepsilon_{\sigma S} + \varepsilon_{\sigma L} = 1 \tag{8.12}$$

Solid phase continuity equation

$$\frac{\partial}{\partial t}\left(\varepsilon_\sigma \langle \rho_\sigma \rangle^\sigma\right) + \nabla \cdot \left(\langle \rho_\sigma \rangle^\sigma \langle \bar{v}_\sigma \rangle\right) + \langle \dot{m}_{sl} \rangle + \langle \dot{m}_{sv} \rangle = 0 \tag{8.13}$$

Solid phase equation of motion (for one dimensional geometry)

$$\langle v_\sigma \rangle^\sigma = \frac{1}{\langle \rho \rangle^\sigma \xi^{n-1}} \int_0^\xi \frac{\partial}{\partial t} \langle \rho_\sigma \rangle d\xi \tag{8.14}$$

Solid phase diffusion equation (for vaporizing component)

$$\frac{\partial}{\partial t}\left(\varepsilon_\sigma \langle \rho_1 \rangle^\sigma\right) + \nabla \cdot \left(\langle \rho_1 \rangle^\sigma \langle \bar{v}_1 \rangle\right) + \langle \dot{m}_{sl} \rangle + \langle \dot{m}_{sv} \rangle = \nabla \cdot \left\{ \langle \rho_\sigma \rangle^\sigma \mathcal{D}_\sigma \nabla \left(\frac{\langle \rho_1 \rangle^\sigma}{\langle \rho_\sigma \rangle^\sigma} \right) \right\} \tag{8.15}$$

Volume constraint

$$\varepsilon_\sigma(t) + \varepsilon_\beta(t) + \varepsilon_\gamma(t) = 1 \tag{8.16}$$

Thermodynamic relations

$$\langle p_1 \rangle^\gamma = \langle \rho_1 \rangle^\gamma R_1 \langle T \rangle \tag{8.17}$$

$$\langle p_2 \rangle^\gamma = \langle \rho_2 \rangle^\gamma R_2 \langle T \rangle \tag{8.18}$$

$$\langle \rho_\gamma \rangle^\gamma = \langle \rho_1 \rangle^\gamma + \langle \rho_2 \rangle^\gamma \tag{8.19}$$

$$\langle p_\gamma \rangle^\gamma = \langle p_1 \rangle^\gamma + \langle p_2 \rangle^\gamma \tag{8.20}$$

If any liquid phase is present, vapor pressure is given by:

$$\langle p_1 \rangle^\gamma = p_1^\circ \exp\left\{-\left[\left(\frac{2\sigma_{\beta\gamma}}{r\rho_\beta R_1 \langle T \rangle}\right) + \frac{\Delta h_{vap}}{R_1}\left(\frac{1}{\langle T \rangle} - \frac{1}{T_\circ}\right)\right]\right\} \text{ or}$$

$$\langle p_1 \rangle^\gamma = p_1^\circ \exp\left\{-\left[\frac{\Delta h_{vap}}{R_1}\left(\frac{1}{\langle T \rangle} - \frac{1}{T_\circ}\right)\right]\right\} \tag{8.21}$$

If the liquid phase is not present, and the liquid component is desorbing from the solid, the reduced vapor pressure in equilibrium with the solid must be used. This relation may be determined directly from the sorption isotherm for the solid:

$$\langle p_1 \rangle^\gamma = f(p_s, \rho_l, \rho_s, \varepsilon_{\sigma L}) \text{ at the temperature } \langle T \rangle, \text{ only } \varepsilon_{\sigma L} \text{ is unknown .} \tag{8.22}$$

Sorption relations (volume average solid equilibrium)

$$Q_{sl} \ (J/kg) = 0.195\left(1 - \frac{\langle p_1 \rangle^\gamma}{p_s}\right)\left(\frac{1}{\left(0.2 + \frac{\langle p_1 \rangle^\gamma}{p_s}\right)} + \frac{1}{\left(1.05 - \frac{\langle p_1 \rangle^\gamma}{p_s}\right)}\right) \tag{8.23}$$

$$\frac{\langle \rho_1 \rangle^\sigma}{\langle \rho_2 \rangle^\sigma} = \frac{\varepsilon_{\sigma l}\rho_l}{(1-\varepsilon_{\sigma l})\rho_s} = R_f\left(0.55\frac{\langle p_1 \rangle^\gamma}{p_s}\right)\left[\frac{1}{\left(0.25 + \frac{\langle p_1 \rangle^\gamma}{p_s}\right)} + \frac{1}{\left(1.25 - \frac{\langle p_1 \rangle^\gamma}{p_s}\right)}\right] \tag{8.24}$$

This is a total of 20 main equations and 20 unknown variables, which should allow for the solution of the set of equations using numerical methods. The 20 unknown variables are:

$$\varepsilon_\sigma, \varepsilon_\beta, \varepsilon_\gamma, \langle \bar{v}_\sigma \rangle, \langle \bar{v}_\beta \rangle, \langle \bar{v}_\gamma \rangle, \langle T \rangle,$$

$$\langle \dot{m}_{sl} \rangle, \langle \dot{m}_{sv} \rangle, \langle \dot{m}_{lv} \rangle, Q_{sl}$$

$$\langle p_\gamma \rangle^\gamma, \langle p_1 \rangle^\gamma, \langle p_2 \rangle^\gamma, \langle \rho_\gamma \rangle^\gamma, \langle \rho_1 \rangle^\gamma, \langle \rho_2 \rangle^\gamma$$

$$\langle \rho_\gamma \rangle^\sigma, \langle \rho_1 \rangle^\sigma, \langle \rho_2 \rangle^\sigma$$

9. Simplification of Total Equation Set

The total equation set is quite complicated. There are several ways to simplify the set of equations, yet still include the modes of energy and mass transport which are important in various situations. First, we will include the the gas phase convection and the liquid phase convection terms, but make several assumptions about the diffusion processes that will simplify the set of equations significantly. Then we will further simplify the set of equations to examine the case where gas phase convection is not present, but liquid capillary transport is important. Finally, we will simplify the set of equations to the situation where mass is only tranported through diffusion in the gas phase.

Simplified equations which include liquid and gas phase convection

The total drying equation set will be simplified by making several assumptions:

1) We will only use the continuity equations to account for the mass transfer of the component which crosses phase boundaries (water). This means we will only use the species continuity and diffusion equations for component 1.

2) We will use the diffusion coefficients for water in the solid and water in air, and ignore the counterdiffusion of air through the water vapor, etc. We will assume these diffusion coefficients are constant.

3) For the diffusion equations, we will assume that the density of the inert phase (solid or air) is constant during the diffusion process.

4) We will ignore the swelling velocity of the solid phase, but will the include the change in volume of the solid as water is absorbed.

5) We will assume transport only in one dimension (x).

Total thermal energy equation

$$\langle \rho \rangle C_p \frac{\partial \langle T \rangle}{\partial t} + \left[\begin{array}{c} \rho_\beta (c_p)_\beta \langle v_{\beta x} \rangle \\ + (c_p)_1 \langle \rho_1 v_{1x} \rangle \end{array} \right] \frac{\partial \langle T \rangle}{\partial x} + \left[\begin{array}{c} \Delta h_{vap} \langle \dot{m}_{lv} \rangle \\ + Q_l \langle \dot{m}_{sl} \rangle \\ + (Q_l + \Delta h_{vap}) \langle \dot{m}_{sv} \rangle \end{array} \right] = \frac{\partial}{\partial x} \left[k_{eff} \frac{\partial \langle T \rangle}{\partial x} \right] \tag{9.1}$$

Liquid phase equation of motion

$$\langle v_{\beta x} \rangle = -\left(\frac{K_\beta}{\mu_\beta} \right) \frac{\partial}{\partial x} \left(\langle p_1 \rangle^\gamma + \langle p_2 \rangle^\gamma - P_c \right) \tag{9.2}$$

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Liquid phase continuity equation

$$\frac{\partial \varepsilon_\beta}{\partial t} + \frac{\partial}{\partial x}\langle \bar{v}_\beta \rangle + \frac{(\langle \dot{m}_{lv}\rangle - \langle \dot{m}_{sv}\rangle)}{\rho_\beta} = 0 \tag{9.3}$$

Gas phase equation of motion

$$\langle v_{\gamma x}\rangle = -\left(\frac{K_\gamma}{\mu_\gamma}\right)\frac{\partial}{\partial x}\left(\langle p_1\rangle^\gamma + \langle p_2\rangle^\gamma\right) \tag{9.4}$$

Gas phase continuity equation

$$\frac{\partial}{\partial t}\left(\varepsilon_\gamma \langle \rho_\gamma\rangle^\gamma\right) + \frac{\partial}{\partial x}\left(\langle \rho_\gamma\rangle^\gamma \langle v_{\gamma x}\rangle\right) = \langle \dot{m}_{lv}\rangle + \langle \dot{m}_{sv}\rangle \tag{9.5}$$

Gas phase diffusion equation

$$\frac{\partial}{\partial t}\left(\varepsilon_\gamma \langle \rho_1\rangle^\gamma\right) + \frac{\partial}{\partial x}\left(\langle \rho_1\rangle^\gamma \langle v_{\gamma x}\rangle\right) - \langle \dot{m}_{lv}\rangle - \langle \dot{m}_{sv}\rangle = \frac{\partial}{\partial x}\left[\mathcal{D}_{eff}\frac{\partial}{\partial x}\left(\langle \rho_1\rangle^\gamma\right)\right] \tag{9.6}$$

Solid phase density relations

$$\langle \rho_\sigma\rangle^\sigma = \langle \rho_1\rangle^\sigma + \langle \rho_2\rangle^\sigma \tag{9.7}$$

$$\rho_1 = \varepsilon_{\sigma L}\rho_L \tag{9.8}$$

$$\rho_2 = (1 - \varepsilon_{\sigma L})\rho_S \tag{9.9}$$

$$\varepsilon_{\sigma S} + \varepsilon_{\sigma L} = 1 \tag{9.10}$$

Solid phase continuity equation

$$\frac{\partial}{\partial t}\left(\varepsilon_\sigma \langle \rho_\sigma\rangle^\sigma\right) + \langle \dot{m}_{sl}\rangle + \langle \dot{m}_{sv}\rangle = 0 \tag{9.11}$$

Solid phase diffusion equation

$$\frac{\partial}{\partial t}\left(\varepsilon_\sigma \langle \rho_1\rangle^\sigma\right) + \langle \dot{m}_{sl}\rangle + \langle \dot{m}_{sv}\rangle = \frac{\partial}{\partial x}\left(\mathcal{D}_\sigma \frac{\partial \langle \rho_1\rangle^\sigma}{\partial x}\right) \tag{9.12}$$

Volume constraint

$$\varepsilon_\sigma(t) + \varepsilon_\beta(t) + \varepsilon_\gamma(t) = 1 \tag{9.13}$$

Thermodynamic relations

$$\langle p_1 \rangle^\gamma = \langle \rho_1 \rangle^\gamma R_1 \langle T \rangle \tag{9.14}$$

$$\langle p_2 \rangle^\gamma = \langle \rho_2 \rangle^\gamma R_2 \langle T \rangle \tag{9.15}$$

$$\langle \rho_\gamma \rangle^\gamma = \langle \rho_1 \rangle^\gamma + \langle \rho_2 \rangle^\gamma \tag{9.16}$$

$$\langle p_\gamma \rangle^\gamma = \langle p_1 \rangle^\gamma + \langle p_2 \rangle^\gamma \tag{9.17}$$

If any liquid phase is present, vapor pressure is given by:

$$\langle p_1 \rangle^\gamma = p_1^\circ \exp\left\{ -\left[\left(\frac{2\sigma_{\beta\gamma}}{r\rho_\beta R_1 \langle T \rangle} \right) + \frac{\Delta h_{vap}}{R_1} \left(\frac{1}{\langle T \rangle} - \frac{1}{T_o} \right) \right] \right\} \tag{9.18}$$

$$\text{or } \langle p_1 \rangle^\gamma = p_1^\circ \exp\left\{ -\left[\frac{\Delta h_{vap}}{R_1} \left(\frac{1}{\langle T \rangle} - \frac{1}{T_o} \right) \right] \right\} \tag{9.19}$$

If the liquid phase is not present, and the liquid component is desorbing from the solid, the reduced vapor pressure in equilibrium with the solid must be used. This relation may be determined directly from the sorption isotherm for the solid:

$$\langle p_1 \rangle^\gamma = f(p_s, \rho_l, \rho_s, \varepsilon_{\sigma l}) \text{ at the temperature } \langle T \rangle, \text{ only } \varepsilon_{\sigma l} \text{ is unknown} \tag{9.20}$$

Sorption relations (solid equilibrium)

$$Q_l \ (\text{J}/\text{kg}) = 0.195\left(1 - \frac{\langle p_1 \rangle^\gamma}{p_s} \right)\left(\frac{1}{\left(0.2 + \dfrac{\langle p_1 \rangle^\gamma}{p_s} \right)} + \frac{1}{\left(1.05 - \dfrac{\langle p_1 \rangle^\gamma}{p_s} \right)} \right) \tag{9.21}$$

$$\frac{\langle \rho_1 \rangle^\sigma}{\langle \rho_2 \rangle^\sigma} = \frac{\varepsilon_{\sigma l}\rho_l}{(1-\varepsilon_{\sigma l})\rho_s} = R_f\left(0.55\frac{\langle p_1 \rangle^\gamma}{p_s} \right)\left[\frac{1}{\left(0.25 + \dfrac{\langle p_1 \rangle^\gamma}{p_s} \right)} + \frac{1}{\left(1.25 - \dfrac{\langle p_1 \rangle^\gamma}{p_s} \right)} \right] \tag{9.22}$$

$$k_{eff} = \varepsilon_\sigma \left(\frac{k_1 \rho_1 + k_2 \rho_2}{\rho_1 + \rho_2} \right) + \varepsilon_\beta k_\beta + \varepsilon_\gamma \left(\frac{k_1 \rho_1 + k_2 \rho_2}{\rho_1 + \rho_2} \right) \qquad (9.23)$$

$$\mathcal{D}_{eff} = \frac{\mathcal{D}_a \varepsilon_\gamma}{\tau} \qquad (9.24)$$

$$\langle \rho \rangle = \varepsilon_\sigma \left(\langle \rho_1 \rangle^\sigma + \langle \rho_2 \rangle^\sigma \right) + \varepsilon_\sigma \langle \rho_\beta \rangle^\beta + \varepsilon_\gamma \left(\langle \rho_1 \rangle^\gamma + \langle \rho_2 \rangle^\gamma \right) \qquad (9.25)$$

$$C_p = \frac{\varepsilon_\sigma \left[\langle \rho_1 \rangle^\sigma (c_p)_1 + \langle \rho_2 \rangle^\sigma (c_p)_2 \right] + \varepsilon_\beta \rho_\beta (c_p)_\beta + \varepsilon_\gamma \left[\langle \rho_1 \rangle^\gamma (c_p)_1 + \langle \rho_2 \rangle^\gamma (c_p)_2 \right]}{\langle \rho \rangle} \qquad (9.26)$$

This simplified equation set is now 19 equations for 19 variables, which is enough to solve the set of equations for the following unknown variables:

$$\varepsilon_\sigma, \varepsilon_\beta, \varepsilon_\gamma, \langle \bar{v}_\beta \rangle, \langle \bar{v}_\gamma \rangle, \langle T \rangle,$$

$$\langle \dot{m}_{sl} \rangle, \langle \dot{m}_{sv} \rangle, \langle \dot{m}_{lv} \rangle, Q_{sl}$$

$$\langle p_\gamma \rangle^\gamma, \langle p_1 \rangle^\gamma, \langle p_2 \rangle^\gamma, \langle \rho_\gamma \rangle^\gamma, \langle \rho_1 \rangle^\gamma, \langle \rho_2 \rangle^\gamma,$$

$$\langle \rho_\gamma \rangle^\gamma, \langle \rho_1 \rangle^\gamma, \langle \rho_2 \rangle^\gamma$$

Simplified equations which neglect gas phase convection

The gas phase convection is now neglected, so that the air within the pore spaces is assumed to be stagnant, and mass and energy are transported within the gas phase only by diffusion.

Total thermal energy equation

$$\langle \rho \rangle C_p \frac{\partial \langle T \rangle}{\partial t} + \left[\rho_\beta (c_p)_\beta \langle v_{\beta x} \rangle \right] \frac{\partial \langle T \rangle}{\partial x} + \begin{bmatrix} \Delta h_{vap} \langle \dot{m}_{lv} \rangle \\ + Q_l \langle \dot{m}_{sl} \rangle \\ + (Q_l + \Delta h_{vap}) \langle \dot{m}_{sv} \rangle \end{bmatrix} = \frac{\partial}{\partial x} \left[k_{eff} \frac{\partial \langle T \rangle}{\partial x} \right] \tag{9.27}$$

Liquid phase equation of motion

$$\langle v_{\beta x} \rangle = - \left(\frac{K_\beta}{\mu_\beta} \right) \frac{\partial}{\partial x} \left(\langle p_1 \rangle^\gamma + \langle p_2 \rangle^\gamma - P_c \right) \tag{9.28}$$

Liquid phase continuity equation

$$\frac{\partial \varepsilon_\beta}{\partial t} + \frac{\partial}{\partial x} \langle \bar{v}_\beta \rangle + \frac{(\langle \dot{m}_{lv} \rangle - \langle \dot{m}_{sv} \rangle)}{\rho_\beta} = 0 \tag{9.29}$$

Gas phase continuity equation

$$\frac{\partial}{\partial t} \left(\varepsilon_\gamma \langle \rho_\gamma \rangle^\gamma \right) = \langle \dot{m}_{lv} \rangle + \langle \dot{m}_{sv} \rangle \tag{9.30}$$

Gas phase diffusion equation

$$\frac{\partial}{\partial t} \left(\varepsilon_\gamma \langle \rho_1 \rangle^\gamma \right) - \langle \dot{m}_{lv} \rangle - \langle \dot{m}_{sv} \rangle = \frac{\partial}{\partial x} \left[\mathcal{D}_{eff} \frac{\partial}{\partial x} \left(\langle \rho_1 \rangle^\gamma \right) \right] \tag{9.31}$$

Solid phase density relations

$$\langle \rho_\sigma \rangle^\sigma = \langle \rho_1 \rangle^\sigma + \langle \rho_2 \rangle^\sigma \tag{9.32}$$

$$\rho_1 = \varepsilon_{\sigma L} \rho_L \tag{9.33}$$

$$\rho_2 = (1 - \varepsilon_{\sigma L}) \rho_S \tag{9.34}$$

$$\varepsilon_{\sigma S} + \varepsilon_{\sigma L} = 1 \tag{9.35}$$

Solid phase continuity equation

$$\frac{\partial}{\partial t} \left(\varepsilon_\sigma \langle \rho_\sigma \rangle^\sigma \right) + \langle \dot{m}_{sl} \rangle + \langle \dot{m}_{sv} \rangle = 0 \tag{9.36}$$

Solid phase diffusion equation

$$\frac{\partial}{\partial t} \left(\varepsilon_\sigma \langle \rho_1 \rangle^\sigma \right) + \langle \dot{m}_{sl} \rangle + \langle \dot{m}_{sv} \rangle = \frac{\partial}{\partial x} \left(\mathcal{D}_\sigma \frac{\partial \langle \rho_1 \rangle^\sigma}{\partial x} \right) \tag{9.37}$$

Volume constraint

$$\varepsilon_\sigma(t) + \varepsilon_\beta(t) + \varepsilon_\gamma(t) = 1 \tag{9.38}$$

Thermodynamic relations

$$\langle p_1 \rangle^\gamma = \langle \rho_1 \rangle^\gamma R_1 \langle T \rangle \tag{9.39}$$

$$\langle p_2 \rangle^\gamma = \langle \rho_2 \rangle^\gamma R_2 \langle T \rangle \tag{9.40}$$

$$\langle \rho_\gamma \rangle^\gamma = \langle \rho_1 \rangle^\gamma + \langle \rho_2 \rangle^\gamma \tag{9.41}$$

$$\langle p_\gamma \rangle^\gamma = \langle p_1 \rangle^\gamma + \langle p_2 \rangle^\gamma \tag{9.42}$$

If any liquid phase is present, vapor pressure is given by:

$$\langle p_1 \rangle^\gamma = p_1^\circ \exp\left\{-\left[\left(\frac{2\sigma_{\beta\gamma}}{r\rho_\beta R_1 \langle T \rangle}\right) + \frac{\Delta h_{vap}}{R_1}\left(\frac{1}{\langle T \rangle} - \frac{1}{T_c}\right)\right]\right\} \tag{9.43}$$

$$\text{or } \langle p_1 \rangle^\gamma = p_1^\circ \exp\left\{-\left[\frac{\Delta h_{vap}}{R_1}\left(\frac{1}{\langle T \rangle} - \frac{1}{T_c}\right)\right]\right\} \tag{9.44}$$

If the liquid phase is not present, and the liquid component is desorbing from the solid, the reduced vapor pressure in equilibrium with the solid must be used. This relation may be determined directly from the sorption isotherm for the solid:

$$\langle p_1 \rangle^\gamma = f(p_s, \rho_l, \rho_s, \varepsilon_{\sigma l}) \text{ at the temperature } \langle T \rangle, \text{ only } \varepsilon_{\sigma l} \text{ is unknown} \tag{9.45}$$

Sorption relations (solid equilibrium)

$$Q_l \ (J/kg) = 0.195\left(1 - \frac{\langle p_1 \rangle^\gamma}{p_s}\right)\left(\frac{1}{\left(0.2 + \frac{\langle p_1 \rangle^\gamma}{p_s}\right)} + \frac{1}{\left(1.05 - \frac{\langle p_1 \rangle^\gamma}{p_s}\right)}\right) \tag{9.46}$$

$$\frac{\langle \rho_1 \rangle^\sigma}{\langle \rho_2 \rangle^\sigma} = \frac{\varepsilon_{\sigma l} \rho_l}{(1 - \varepsilon_{\sigma l})\rho_s} = R_f\left(0.55\frac{\langle p_1 \rangle^\gamma}{p_s}\right)\left[\frac{1}{\left(0.25 + \frac{\langle p_1 \rangle^\gamma}{p_s}\right)} + \frac{1}{\left(1.25 - \frac{\langle p_1 \rangle^\gamma}{p_s}\right)}\right] \tag{9.47}$$

$$k_{eff} = \varepsilon_\sigma \left(\frac{k_1 \rho_1 + k_2 \rho_2}{\rho_1 + \rho_2} \right) + \varepsilon_\beta k_\beta + \varepsilon_\gamma \left(\frac{k_1 \rho_1 + k_2 \rho_2}{\rho_1 + \rho_2} \right) \tag{9.48}$$

$$\mathcal{D}_{eff} = \frac{\mathcal{D}_a \varepsilon_\gamma}{\tau} \tag{9.49}$$

$$\langle \rho \rangle = \varepsilon_\sigma \left(\langle \rho_1 \rangle^\sigma + \langle \rho_2 \rangle^\sigma \right) + \varepsilon_s \langle \rho_\beta \rangle^\beta + \varepsilon_\gamma \left(\langle \rho_1 \rangle^\gamma + \langle \rho_2 \rangle^\gamma \right) \tag{9.50}$$

$$C_p = \frac{\varepsilon_\sigma \left[\langle \rho_1 \rangle^\sigma (c_p)_1 + \langle \rho_2 \rangle^\sigma (c_p)_2 \right] + \varepsilon_\beta \rho_\beta (c_p)_\beta + \varepsilon_\gamma \left[\langle \rho_1 \rangle^\gamma (c_p)_1 + \langle \rho_2 \rangle^\gamma (c_p)_2 \right]}{\langle \rho \rangle} \tag{9.51}$$

This simplified equation set is now 18 equations for 18 variables, which is enough to solve the set of equations for the following unknown variables:

$\varepsilon_\sigma, \varepsilon_\beta, \varepsilon_\gamma, \langle \tilde{v}_\beta \rangle, \langle T \rangle,$

$\langle \dot{m}_{sl} \rangle, \langle \dot{m}_{sv} \rangle, \langle \dot{m}_{lv} \rangle, Q_{sl}$

$\langle p_\gamma \rangle^\gamma, \langle p_1 \rangle^\gamma, \langle p_2 \rangle^\gamma, \langle \rho_\gamma \rangle^\gamma, \langle \rho_1 \rangle^\gamma, \langle \rho_2 \rangle^\gamma,$

$\langle \rho_\gamma \rangle^\gamma, \langle \rho_1 \rangle^\gamma, \langle \rho_2 \rangle^\gamma$

Simplified equations which neglect both liquid and gas phase convection

Both liquid phase capillary transport, and gas phase convection are neglected, so that mass and energy are transported within the gas phase only by diffusion, and the liquid which condenses at a particular point within the material does not wick or flow away from that point, but accumulates over time. The liquid may be absorbed into the solid phase, or it may evaporate at a later time, but it may only be transported through the structure by going into the vapor phase.

Total thermal energy equation

$$\langle \rho \rangle C_p \frac{\partial \langle T \rangle}{\partial t} + \begin{bmatrix} \Delta h_{vap} \langle \dot{m}_{lv} \rangle \\ + Q_l \langle \dot{m}_{sl} \rangle \\ + (Q_l + \Delta h_{vap}) \langle \dot{m}_{sv} \rangle \end{bmatrix} = \frac{\partial}{\partial x} \left[k_{eff} \frac{\partial \langle T \rangle}{\partial x} \right] \tag{9.52}$$

Liquid phase continuity equation

$$\frac{\partial \varepsilon_\beta}{\partial t} + \frac{(\langle \dot{m}_{lv} \rangle - \langle \dot{m}_{sv} \rangle)}{\rho_\beta} = 0 \tag{9.53}$$

Gas phase continuity equation

$$\frac{\partial}{\partial t} \left(\varepsilon_\gamma \langle \rho_\gamma \rangle^\gamma \right) = \langle \dot{m}_{lv} \rangle + \langle \dot{m}_{sv} \rangle \tag{9.54}$$

Gas phase diffusion equation

$$\frac{\partial}{\partial t} \left(\varepsilon_\gamma \langle \rho_1 \rangle^\gamma \right) - \langle \dot{m}_{lv} \rangle - \langle \dot{m}_{sv} \rangle = \frac{\partial}{\partial x} \left[\mathcal{D}_{eff} \frac{\partial}{\partial x} \left(\langle \rho_1 \rangle^\gamma \right) \right] \tag{9.55}$$

Solid phase density relations

$$\langle \rho_\sigma \rangle^\sigma = \langle \rho_1 \rangle^\sigma + \langle \rho_2 \rangle^\sigma \tag{9.56}$$

$$\rho_1 = \varepsilon_{\sigma L} \rho_L \tag{9.57}$$

$$\rho_2 = (1 - \varepsilon_{\sigma L}) \rho_S \tag{9.58}$$

$$\varepsilon_{\sigma S} + \varepsilon_{\sigma L} = 1 \tag{9.59}$$

Solid phase continuity equation

$$\frac{\partial}{\partial t} \left(\varepsilon_\sigma \langle \rho_\sigma \rangle^\sigma \right) + \langle \dot{m}_{sl} \rangle + \langle \dot{m}_{sv} \rangle = 0 \tag{9.60}$$

Solid phase diffusion equation

$$\frac{\partial}{\partial t} \left(\varepsilon_\sigma \langle \rho_1 \rangle^\sigma \right) + \langle \dot{m}_{sl} \rangle + \langle \dot{m}_{sv} \rangle = \frac{\partial}{\partial x} \left(\mathcal{D}_\sigma \frac{\partial \langle \rho_1 \rangle^\sigma}{\partial x} \right) \tag{9.61}$$

Volume constraint

$$\varepsilon_\sigma(t) + \varepsilon_\beta(t) + \varepsilon_\gamma(t) = 1 \tag{9.62}$$

Thermodynamic relations

$$\langle p_1 \rangle^\gamma = \langle \rho_1 \rangle^\gamma R_1 \langle T \rangle \tag{9.63}$$

$$\langle p_2 \rangle^\gamma = \langle \rho_2 \rangle^\gamma R_2 \langle T \rangle \tag{9.64}$$

$$\langle \rho_\gamma \rangle^\gamma = \langle \rho_1 \rangle^\gamma + \langle \rho_2 \rangle^\gamma \tag{9.65}$$

$$\langle p_\gamma \rangle^\gamma = \langle p_1 \rangle^\gamma + \langle p_2 \rangle^\gamma \tag{9.66}$$

If any liquid phase is present, vapor pressure is given by:

$$\langle p_1 \rangle^\gamma = p_1^\circ \exp\left\{ -\left[\left(\frac{2\sigma_{\beta\gamma}}{r\rho_\beta R_1 \langle T \rangle} \right) + \frac{\Delta h_{vap}}{R_1} \left(\frac{1}{\langle T \rangle} - \frac{1}{T_\circ} \right) \right] \right\} \tag{9.67}$$

$$\text{or } \langle p_1 \rangle^\gamma = p_1^\circ \exp\left\{ -\left[\frac{\Delta h_{vap}}{R_1} \left(\frac{1}{\langle T \rangle} - \frac{1}{T_\circ} \right) \right] \right\} \tag{9.68}$$

If the liquid phase is not present, and the liquid component is desorbing from the solid, the reduced vapor pressure in equilibrium with the solid must be used. This relation may be determined directly from the sorption isotherm for the solid:

$$\langle p_1 \rangle^\gamma = f(p_s, \rho_l, \rho_s, \varepsilon_{\sigma l}) \text{ at the temperature } \langle T \rangle \text{ , only } \varepsilon_{\sigma l} \text{ is unknown} \tag{9.69}$$

$$Q_l \text{ (J / kg)} = 0.195\left(1 - \frac{\langle p_1 \rangle^\gamma}{p_s} \right)\left(\frac{1}{\left(0.2 + \dfrac{\langle p_1 \rangle^\gamma}{p_s} \right)} + \frac{1}{\left(1.05 - \dfrac{\langle p_1 \rangle^\gamma}{p_s} \right)} \right) \tag{9.70}$$

$$\frac{\langle \rho_1 \rangle^\sigma}{\langle \rho_2 \rangle^\sigma} = \frac{\varepsilon_{\sigma l}\rho_l}{(1 - \varepsilon_{\sigma l})\rho_s} = R_f\left(0.55\frac{\langle p_1 \rangle^\gamma}{p_s} \right)\left[\frac{1}{\left(0.25 + \dfrac{\langle p_1 \rangle^\gamma}{p_s} \right)} + \frac{1}{\left(1.25 - \dfrac{\langle p_1 \rangle^\gamma}{p_s} \right)} \right] \tag{9.71}$$

$$k_{eff} = \varepsilon_\sigma\left(\frac{k_1\rho_1 + k_2\rho_2}{\rho_1 + \rho_2}\right) + \varepsilon_\beta k_\beta + \varepsilon_\gamma\left(\frac{k_1\rho_1 + k_2\rho_2}{\rho_1 + \rho_2}\right) \tag{9.72}$$

$$\mathcal{D}_{eff} = \frac{\mathcal{D}_a \varepsilon_\gamma}{\tau} \tag{9.73}$$

$$\langle\rho\rangle = \varepsilon_\sigma\left(\langle\rho_1\rangle^\sigma + \langle\rho_2\rangle^\sigma\right) + \varepsilon_\sigma\langle\rho_\beta\rangle^\beta + \varepsilon_\gamma\left(\langle\rho_1\rangle^\gamma + \langle\rho_2\rangle^\gamma\right) \tag{9.74}$$

$$C_p = \frac{\varepsilon_\sigma\left[\langle\rho_1\rangle^\sigma(c_p)_1 + \langle\rho_2\rangle^\sigma(c_p)_2\right] + \varepsilon_\beta\rho_\beta(c_p)_\beta + \varepsilon_\gamma\left[\langle\rho_1\rangle^\gamma(c_p)_1 + \langle\rho_2\rangle^\gamma(c_p)_2\right]}{\langle\rho\rangle} \tag{9.75}$$

This simplified equation set is now 17 equations for 17 variables (the sorption equation and the solid-vapor pressure equation are a duplicate), which are enough to solve the set of equations for the following unknown variables:

$\varepsilon_\sigma, \varepsilon_\beta, \varepsilon_\gamma, \langle T\rangle,$

$\langle\dot{m}_{sl}\rangle, \langle\dot{m}_{sv}\rangle, \langle\dot{m}_{lv}\rangle, Q_{sl}$

$\langle p_\gamma\rangle^\gamma, \langle p_1\rangle^\gamma, \langle p_2\rangle^\gamma, \langle\rho_\gamma\rangle^\gamma, \langle\rho_1\rangle^\gamma, \langle\rho_2\rangle^\gamma,$

$\langle\rho_\gamma\rangle^\gamma, \langle\rho_1\rangle^\gamma, \langle\rho_2\rangle^\gamma$

10. Comparison with Previously-Derived Equations

The simplified sytems of partial differential equations given in the previous chapter still contain many equations with a large number of unknown variables. Even for the simplified case of vapor diffusion, the system of equations is quite confusing, and it is difficult to verify their accuracy, other than by checking for dimensional consistency. One way of checking their validity is to see if they simplify down to more well-known diffusion equations for the transport of water vapor in air through a porous hygroscopic solid. Such a system of equations has been well documented by Henry[12], Norden and David[9], and Li and Holcombe[13], who have used them to describe the diffusion of water vapor through a hygroscopic porous material.

We will make the same assumptions used by these previous workers, and attempt to transform the system of equations for the case of vapor diffusion (no liquid or gas phase convection) to their system of equations. For completeness, we will also need to write the various equations in terms of the variables and units used their work.

The major simplifying assumptions are: 1) there is no liquid or gas phase convection, 2) there is no liquid phase present, 3) the heat capacity of the gas phase can be neglected, 4) the volume of the solid remains constant and does not swell, 5) the solid and gas phase volume fractions are both constant, 6) the thermal conductivity tensor may be expressed as a constant scalar thermal conductivity coefficient, 7) the gas phase diffusion coefficient is constant, 7) the transport is one-dimensional (x-direction).

The total thermal energy equation becomes:

$$\langle \rho \rangle C_p \frac{\partial \langle T \rangle}{\partial t} + \left(Q_l + \Delta h_{vap} \right)\langle \dot{m}_{sv} \rangle = \nabla \cdot \left(K_{eff}^T \cdot \nabla \langle T \rangle \right)$$ (10.1)

or

$$\langle \rho \rangle C_p \frac{\partial \langle T \rangle}{\partial t} + \left(Q_l + \Delta h_{vap} \right)\langle \dot{m}_{sv} \rangle = k_{eff} \frac{\partial^2 \langle T \rangle}{\partial x^2}$$ (10.2)

The gas phase continuity equation becomes:

$$\varepsilon_\gamma \frac{\partial}{\partial t}\left(\langle \rho_\gamma \rangle^\gamma \right) = \langle \dot{m}_{sv} \rangle$$ (10.3)

The gas phase diffusion equation (component 1--water vapor):

$$\varepsilon_\gamma \frac{\partial}{\partial t}\left(\langle \rho_1 \rangle^\gamma \right) - \langle \dot{m}_{sv} \rangle = \nabla \cdot \left\{ \langle \rho_\gamma \rangle^\gamma \mathcal{D}_{eff} \nabla \left(\frac{\langle \rho_1 \rangle^\gamma}{\langle \rho_\gamma \rangle^\gamma} \right) \right\}$$ (10.4)

or

$$\varepsilon_\gamma \frac{\partial}{\partial t}\left(\langle \rho_1 \rangle^\gamma \right) - \langle \dot{m}_{sv} \rangle = \mathcal{D}_{eff} \frac{\partial^2 \langle \rho_1 \rangle^\gamma}{\partial x^2}$$ (10.5)

The solid phase continuity equation (component 1--water):

$$\varepsilon_\sigma \frac{\partial}{\partial t}\left(\langle \rho_1 \rangle^\sigma\right) + \langle \dot{m}_{sv} \rangle = 0 \tag{10.6}$$

For the solid phase diffusion equation (component 1--water) we assume that the diffusional transport through the solid phase is insignificant compared to the diffusion through the gas phase, so the diffusion equation reduces to the continuity equation:

$$\varepsilon_\sigma \frac{\partial}{\partial t}\left(\langle \rho_1 \rangle^\sigma\right) + \langle \dot{m}_{sv} \rangle = \nabla \cdot \left\{ \langle \rho_\sigma \rangle^\sigma \mathcal{D}_\sigma \nabla \left(\frac{\rho_1}{\langle \rho_\sigma \rangle^\sigma} \right) \right\} = 0 \tag{10.7}$$

Volume fraction constraint

$$\varepsilon_\gamma + \varepsilon_\sigma = 1 \quad ; \quad \varepsilon_\sigma = 1 - \varepsilon_\gamma \tag{10.8}$$

Thermodynamic relations

$$\langle p_1 \rangle^\gamma = \langle \rho_1 \rangle^\gamma R_1 \langle T \rangle \tag{10.9}$$

$$\langle p_2 \rangle^\gamma = \langle \rho_2 \rangle^\gamma R_2 \langle T \rangle \tag{10.10}$$

$$\langle \rho_\gamma \rangle^\gamma = \langle \rho_1 \rangle^\gamma + \langle \rho_2 \rangle^\gamma \tag{10.11}$$

$$\langle p_\gamma \rangle^\gamma = \langle p_1 \rangle^\gamma + \langle p_2 \rangle^\gamma \tag{10.12}$$

We made the assumption that the mass transport through the solid phase is negligible compared to mass transport through the gas phase. This is reasonable since the diffusion coefficient for water in a solid is always much less than the diffusion coefficient of water vapor through air. We thus only have accumulation of water in the solid, and the solid acts as a source or sink for water vapor.

We can combine the continuity equations for water (component 1) for both phases by connecting the phase equations through the mass flux from the solid to the gas phase:

$$\varepsilon_\sigma \frac{\partial}{\partial t}\left(\langle \rho_1 \rangle^\sigma\right) + \langle \dot{m}_{sv} \rangle = 0 \tag{10.13}$$

$$\varepsilon_\gamma \frac{\partial}{\partial t}\left(\langle \rho_1 \rangle^\gamma\right) - \langle \dot{m}_{sv} \rangle = \mathcal{D}_{eff} \frac{\partial^2 \langle \rho_1 \rangle^\gamma}{\partial x^2} \tag{10.14}$$

$$\left[\varepsilon_\sigma \frac{\partial}{\partial t}\left(\langle \rho_1 \rangle^\sigma\right) + \langle \dot{m}_{sv} \rangle \right] + \left[\varepsilon_\gamma \frac{\partial}{\partial t}\left(\langle \rho_1 \rangle^\gamma\right) - \langle \dot{m}_{sv} \rangle \right] = \mathcal{D}_{eff} \frac{\partial^2 \langle \rho_1 \rangle^\gamma}{\partial x^2} \quad , \tag{10.15}$$

which we may rewrite in terms of the gas phase volume fraction as:

$$\left(1 - \varepsilon_\gamma\right) \frac{\partial}{\partial t}\left(\langle \rho_1 \rangle^\sigma\right) + \varepsilon_\gamma \frac{\partial}{\partial t}\left(\langle \rho_1 \rangle^\gamma\right) = \mathcal{D}_{eff} \frac{\partial^2 \langle \rho_1 \rangle^\gamma}{\partial x^2} \tag{10.16}$$

Through these various assumptions, we have reduced our large equation set down to two main equations for the energy balance and the mass balance:

$$\langle\rho\rangle C_p \frac{\partial\langle T\rangle}{\partial t} + \left(Q_l + \Delta h_{vap}\right)\langle\dot{m}_{sv}\rangle = k_{eff}\frac{\partial^2\langle T\rangle}{\partial x^2} \tag{10.17}$$

$$\left(1-\varepsilon_\gamma\right)\frac{\partial}{\partial t}\left(\langle\rho_1\rangle^\sigma\right) + \varepsilon_\gamma\frac{\partial}{\partial t}\left(\langle\rho_1\rangle^\gamma\right) = \mathcal{D}_{eff}\frac{\partial^2\langle\rho_1\rangle^\gamma}{\partial x^2} \tag{10.18}$$

To make the comparison with the existing equations of Henry[12], Norden and David[9], and Li and Holcombe[13], easier, we can rewrite the intrinsic phase averages in terms of the concentration of water in the solid (C_F) and concentration of water in the gas phase (C):

$$C_F = \frac{\text{mass of water in solid phase}}{\text{solid phase volume}} = \frac{m_{1\sigma}}{V_\sigma} = \rho_{1\sigma} \tag{10.19}$$

$$C = \frac{\text{mass of water in gas phase}}{\text{gas phase volume}} = \frac{m_{1\gamma}}{V_\gamma} = \rho_{1\gamma} \tag{10.20}$$

Since the definition of intrinsic phase average gives the same quantity as the true point value, we may use the fact that

$$\langle\rho_1\rangle^\sigma = \langle C_F\rangle^\sigma = C_F \tag{10.21}$$

$$\langle\rho_1\rangle^\gamma = \langle C\rangle^\gamma = C \tag{10.22}$$

to rewrite the mass balance equation as:

$$\left(1-\varepsilon_\gamma\right)\frac{\partial C_F}{\partial t} + \varepsilon_\gamma\frac{\partial C}{\partial t} = \mathcal{D}_{eff}\frac{\partial^2 C}{\partial x^2} \tag{10.23}$$

We can rewrite the effective diffusion coefficient by using the diffusion coefficient for water vapor in air modified by the gas volume fraction and the tortuosity of the gas volume fraction:

$$\left(1-\varepsilon_\gamma\right)\frac{\partial C_F}{\partial t} + \varepsilon_\gamma\frac{\partial C}{\partial t} = \frac{D_a\varepsilon_\gamma}{\tau}\frac{\partial^2 C}{\partial x^2} \tag{10.24}$$

The thermal energy equation

$$\langle\rho\rangle C_p \frac{\partial\langle T\rangle}{\partial t} + \left(Q_l + \Delta h_{vap}\right)\langle\dot{m}_{sv}\rangle = k_{eff}\frac{\partial^2\langle T\rangle}{\partial x^2} \tag{10.25}$$

may also be modified by recognizing that the mass flux term is contained in the solid phase continuity equation:

$$\varepsilon_\sigma\frac{\partial}{\partial t}\left(\langle\rho_1\rangle^\sigma\right) + \langle\dot{m}_{sv}\rangle = 0 \quad\Rightarrow\quad \langle\dot{m}_{sv}\rangle = -\varepsilon_\sigma\frac{\partial C_F}{\partial t} \tag{10.26}$$

so that the thermal energy equation may be rewritten as:

$$\langle\rho\rangle C_p \frac{\partial\langle T\rangle}{\partial t} - \left(Q_l + \Delta h_{vap}\right)\varepsilon_\sigma\frac{\partial C_F}{\partial t} = k_{eff}\frac{\partial^2\langle T\rangle}{\partial x^2} \tag{10.27}$$

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If we go back to our definitions for the mass fraction weighted average heat capacity,

$$C_p = \frac{\varepsilon_\sigma \sum_{j=1}^{j=N} \langle \rho_j \rangle^\sigma (c_p)_j + \varepsilon_\gamma \sum_{i=1}^{i=N} \langle \rho_i \rangle^\gamma (c_p)_i}{\langle \rho \rangle} \tag{10.28}$$

and spatial average density,

$$\langle \rho \rangle = \varepsilon_\sigma \sum_{j=1}^{j=N} \langle \rho_j \rangle^\sigma + \varepsilon_\gamma \sum_{i=1}^{i=N} \langle \rho_i \rangle^\gamma \tag{10.29}$$

the thermal energy equation may be rewritten as:

$$\varepsilon_\sigma \left[\langle \rho_1 \rangle^\sigma (c_p)_1 + \langle \rho_2 \rangle^\sigma (c_p)_2 \right] + \varepsilon_\gamma \left[\langle \rho_1 \rangle^\gamma (c_p)_1 + \langle \rho_2 \rangle^\gamma (c_p)_2 \right] \frac{\partial \langle T \rangle}{\partial t} \tag{10.30}$$

$$-(Q_l + \Delta h_{vap}) \varepsilon_\sigma \frac{\partial C_F}{\partial t} = k_{eff} \frac{\partial^2 \langle T \rangle}{\partial x^2} \tag{10.31}$$

If we make the assumption that the heat capacity of the gas phase is negligible, then the thermal energy equation becomes:

$$\varepsilon_\sigma \left[\langle \rho_1 \rangle^\sigma (c_p)_1 + \langle \rho_2 \rangle^\sigma (c_p)_2 \right] \frac{\partial \langle T \rangle}{\partial t} - (Q_l + \Delta h_{vap}) \varepsilon_\sigma \frac{\partial C_F}{\partial t} = k_{eff} \frac{\partial^2 \langle T \rangle}{\partial x^2} \quad , \tag{10.31}$$

or dividing through by the solid volume fraction:

$$\left[\langle \rho_1 \rangle^\sigma (c_p)_1 + \langle \rho_2 \rangle^\sigma (c_p)_2 \right] \frac{\partial \langle T \rangle}{\partial t} - (Q_l + \Delta h_{vap}) \frac{\partial C_F}{\partial t} = \frac{k_{eff}}{\varepsilon_\sigma} \frac{\partial^2 \langle T \rangle}{\partial x^2} \tag{10.32}$$

For consistent nomenclature with Li and Holcombe[14] we will write the effective thermal conductivity k_{eff} as K.

We can also define a volumetric heat capacity C_v as:

$$C_v \left(\frac{J}{m^3 \cdot K} \right) = \langle \rho_1 \rangle^\sigma (c_p)_1 + \langle \rho_2 \rangle^\sigma (c_p)_2$$

Units for $\langle \rho_j \rangle^\sigma (c_p)_j$ are $\left(\frac{kg}{m^3} \right) \left(\frac{J}{kg \cdot K} \right) \Rightarrow \left(\frac{J}{m^3 \cdot K} \right)$ \tag{10.33}

The final thermal energy equation reduces to:

$$C_v \frac{\partial \langle T \rangle}{\partial t} - (Q_l + \Delta h_{vap}) \frac{\partial C_F}{\partial t} = K \frac{\partial^2 \langle T \rangle}{\partial x^2} \tag{10.34}$$

The two simplified equations for the mass and energy balance are thus:

$$\left(1-\varepsilon_\gamma\right)\frac{\partial C_F}{\partial t}+\varepsilon_\gamma\frac{\partial C}{\partial t}=\frac{D_a\varepsilon_\gamma}{\tau}\frac{\partial^2 C}{\partial x^2} \tag{10.35}$$

$$C_v\frac{\partial\langle T\rangle}{\partial t}-\left(Q_l+\Delta h_{vap}\right)\frac{\partial C_F}{\partial t}=K\frac{\partial^2\langle T\rangle}{\partial x^2} \tag{10.36}$$

These two simplified equations are very encouraging, since they are exactly the same as previous equations derived by Henry[12], Norden and David[9], and Li and Holcombe[13] for describing the diffusion of water vapor through a hygroscopic porous material. In their equations they define the heat of sorption from the vapor phase into the solid (which is the opposite of the heat of desorption which we used) as:

$$\lambda=\left(Q_l+\Delta h_{vap}\right) \tag{10.37}$$

so that their equations are:

$$\left(1-\varepsilon_\gamma\right)\frac{\partial C_F}{\partial t}+\varepsilon_\gamma\frac{\partial C}{\partial t}=\frac{D_a\varepsilon_\gamma}{\tau}\frac{\partial^2 C}{\partial x^2} \tag{10.38}$$

$$C_v\frac{\partial\langle T\rangle}{\partial t}-\lambda\frac{\partial C_F}{\partial t}=K\frac{\partial^2\langle T\rangle}{\partial x^2} \tag{10.39}$$

11. Conclusions

Whitaker's theory of coupled heat and mass transfer through porous media was modified to include hygroscopic porous materials which can absorb liquid into the solid matrix. The system of equations described in this report should make it possible to evaluate the time-dependent transport properties of hygroscopic and non-hygroscopic clothing materials by including many important factors which are usually ignored in the analysis of heat and mass transfer through textile materials. The set of equations allows for the unsteady capillary wicking of sweat through fabric structure, condensation and evaporation of sweat within various layers of the clothing system, forced gas phase convection through the porous structure of a textile layer, and the swelling and shrinkage of fibers and yarns as they absorb/desorb liquid water and water vapor.

The simplified set of equations for heat and mass transport, where mass transport occurs due to diffusion within the air spaces of the porous solid, was shown to reduce to the well-known coupled heat and mass transfer models for hygroscopic fabrics, as exemplified by the work of Li and Holcombe[14].

Work is underway to develop a numerical code to solve the various sets of equations by standard numerical methods based on Patankar's control volume approach[14]. The numerical method is similar to those developed by Whitaker and Vafai[15], and Tao, Besant, and Rezkallah[16,17,18], which have had success in modeling the unsteady coupled heat and mass transfer process in fibrous insulation materials.

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